VOL. LII NO. 9, SEPTEMBER, 1957

THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LII SEPTEMBER 1957 No. 9

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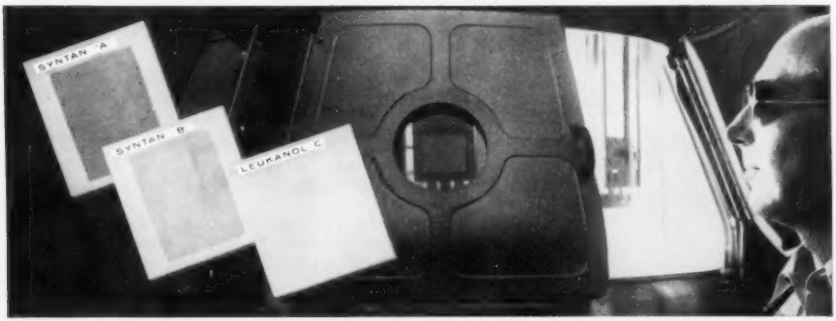

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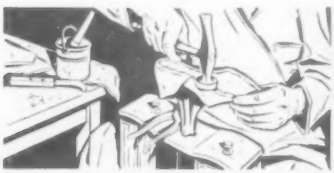

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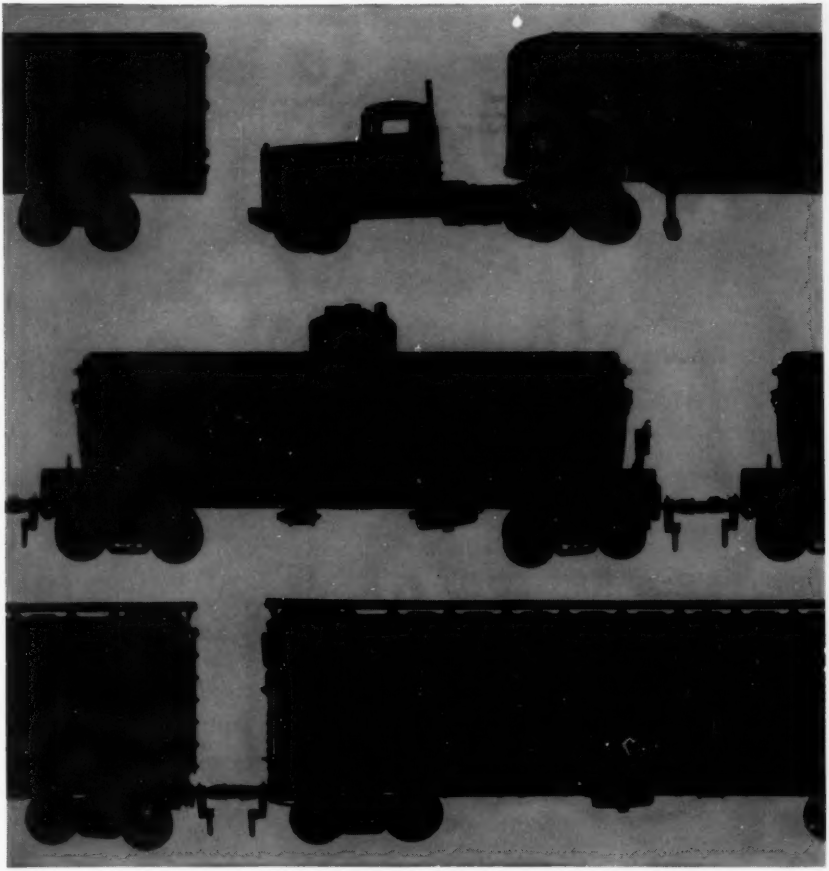

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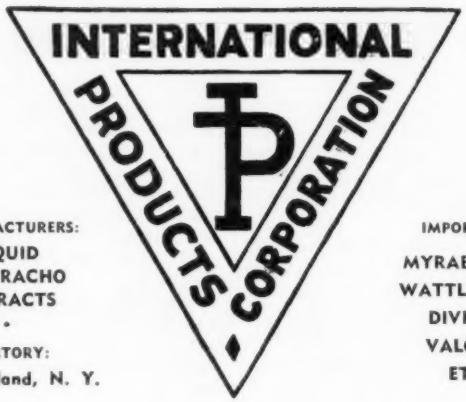

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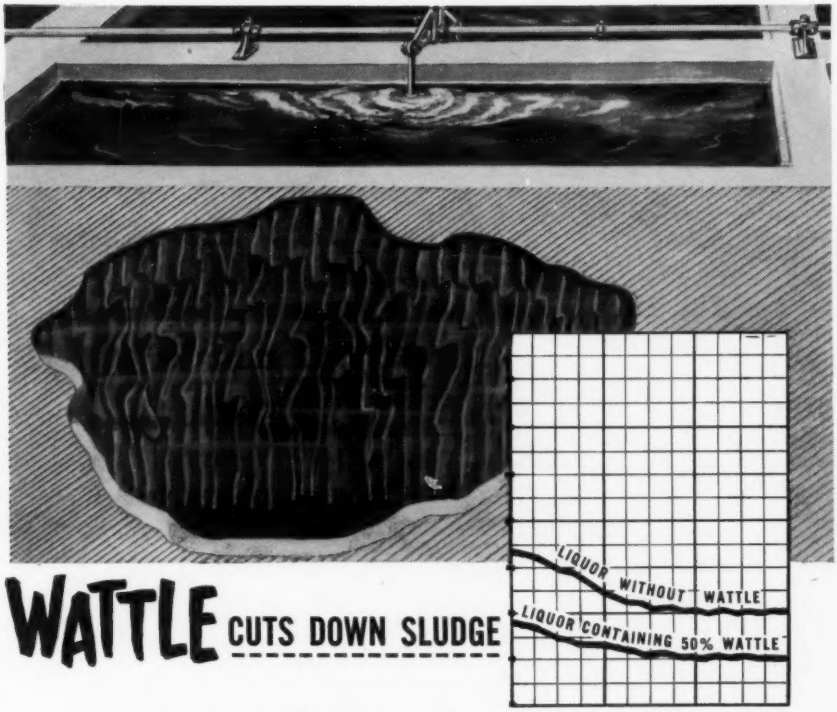

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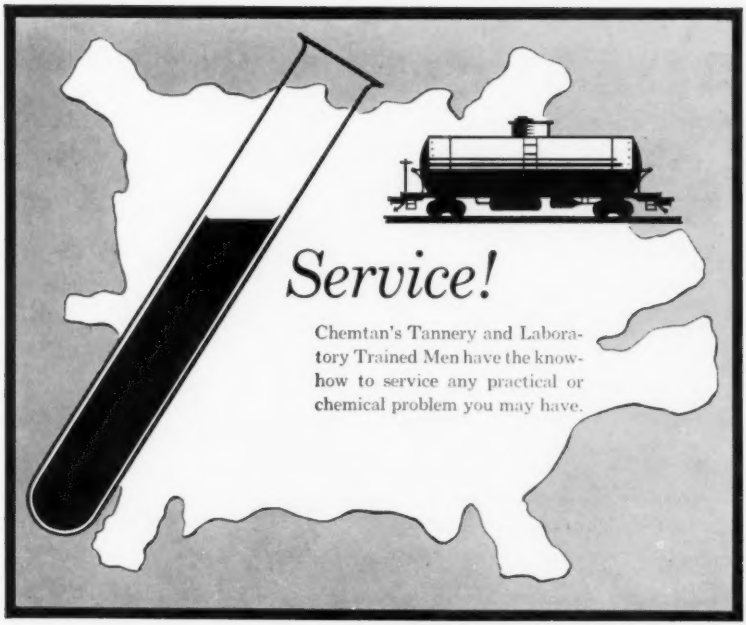
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STUDIES ON THE SIGNIFICANCE OF ANIONIC CHROME IN CHROME TANNING USING RADIOACTIVE ^{51}Cr

AKIRA KAWAMURA and KEIZO WADA

Tokyo Noko Daigaku
(Tokyo University of Agriculture and Technology)
Tokyo, Japan

ABSTRACT

An oxalatochromium compound, containing both cationic and anionic chromium, was prepared in such a manner that the anionic chromium was labelled with radioactive ^{51}Cr. After this compound was aged in solution, the ratio of anionic to cationic chromium did not change, but a considerable part of the radioactivity was found in the cationic part of the molecule, which indicates that a part of the chromium that was anionic originally became cationic because of transfer of oxalate ions to the formerly cationic part of the molecule. In tanning experiments with gelatin blocks the mixed cationic-anionic chromium compound behaved like a purely cationic chromium compound. However, determination of radioactivity of the chromium combined with the gelatin showed that from 60% to 90% of the combined chromium was originally anionic. The bearing of these findings on the theory of chrome tanning is discussed.

INTRODUCTION

Chrome tanning is performed by the joint action of chromium complexes of different charges. It has been, therefore, an important problem for a long time to clarify the action of each complex on protein.

Gustavson (1) stated that collagen tanned by basic chromium sulfate absorbs almost the same amount of anionic complexes, but not cationic, and also that the quantity of vegetable tannins absorbed by collagen decreases when it is pretanned with anionic complexes and increases in the case of pretannage with cationic chrome (2). Otto (3) discussed chrome liquors in relation to the actions of acidic and basic groups of hide, on the basis of experiments on the adsorption of dyes by chrome leathers. Previously, Wilson (4) stated that the isoelectric point of collagen combined with anionic chrome is pH 4.0 but that cationic chrome tannage changes the isoelectric point to pH 7.0. These findings were lately supported by

physicochemical experiments by Petri and Staverman (5) and also by microelectrophoresis determinations (6). The results of these studies showed that anionic chromium always acts on the basic groups of protein.

On the other hand, Stiasny and Lochmann (7) considered that the tanning properties of chromium are controlled by the structure of the complexes (number of water molecules, kinds of radicals coordinated with Cr, size of complex, etc.), and concluded that the sign of charge of the complex was of secondary importance. Sykes (8) and Shuttleworth (9, 10) consider that chrome tanning results from the coordination of carboxyl radicals of protein into the Cr nucleus and that the charge of the Cr complex is not important. The reason for their neglect of the sign of the charge may be attributed to the fact that they consider that all the chromium is fixed to collagen by coordinative bonds as the result of the displacement of acid residues in the Cr complex, with the exception of especially stable groups, by collagen carboxyl groups.

According to the observations of Merrill and Niedercorn (11), leathers that have been tanned with ordinary chromium sulfate contain SO_4 groups of different degrees of stability. Gustavson (12) also discussed the possibility of dividing the SO_4 groups in 33% acid chromium sulfate into two categories with respect to stability of coordination in the complex. The more stable form is thought to be cross-linked between two Cr atoms, while the less stable is combined with one Cr atom only. Gustavson found (13) that when a cationic chrome liquor of 33% acidity, corresponding to the average formula $[Cr_4(OH)_4(SO_4)_2]^{4+}$, was treated with a carboxylic exchange resin, about half of the coordinated SO_4 was displaced by carboxyls, and the other half remained coordinately bound to Cr. However, when the same chrome liquor was treated with collagen, no such displacement of SO_4 occurred.

In order to ascertain the significance of anionic chromium in tanning, the authors synthesized anionic Cr complexes labelled with ^{51}Cr, examined the changes taking place in these complexes during aging, and studied their reactions with protein, employing gelatin gels. The results obtained are reported in this paper.

PREPARATION OF MATERIALS

Five chromium compounds were used in this work: (1) hexaquochromium perchlorate, $[Cr(H_2O)_6](ClO_4)_3$ (cationic); (2) tetraaquooxalatochromium perchlorate, $[CrOx(H_2O)_4]ClO_4$ (cationic); (3) potassium dioxalatochromiate, $K[CrOx_2(H_2O)_2]$ (anionic); (4) potassium trioxalatochromiate, $K_3[CrOx_3]$ (anionic); and (5) the complex cationic-anionic chromium compound, $[CrOx(H_2O)_4][CrOx_2(H_2O)_2]$. In these and other formulas used in this paper Ox stands for the oxalate ion. The first, third, and fourth of the above compounds were synthesized by well known methods.

Previously the authors (14) synthesized the compound $[Cr(H_2O)_6][CrOx_2]$ by passing potassium trioxalatochromiate through Amberlite IR-120-B to remove potassium and reacting the product with hexaquochromium sulfate in the presence of $Ba(OH)_2$ to precipitate the sulfate ions. The product is unstable: on aging in solution, part of the oxalate ions migrate to the cationic side, giving a large proportion of ions with low electrical charge according to the equation:

$$[Cr(H_2O)_6]\ [CrOx_2] \xrightarrow{\text{aging}} [CrOx(H_2O)_4]\ [CrOx_2(H_2O)_2]$$

The product of the above reaction does not change on further aging, as has been proved qualitatively by an electrochromatographic method (14) and quantitatively by ion exchange analysis (15). However, a complex that changes its charge on aging is unsuitable for studying the part played by anionic chromium in tanning. Therefore, the compound $[CrOx(H_2O)_4][CrOx_2(H_2O)_2]$ was synthesized directly by another procedure. Actually two preparations were carried out, in one of which the anionic part was labelled with ^{51}Cr (designated hereafter as Cr*), while the other contained only ordinary Cr. The labelled preparation was used for the work reported in Tables II and IV and the nonlabelled preparation in the work reported in Tables III, V, and VI.

First $[CrOx(H_2O)_4]ClO_4$ and K $[CrOx_2(H_2O)_2]$, or K $[Cr^*Ox_2(H_2O)_2]$, were prepared separately. The former was prepared by treating hexaquochromium sulfate with barium perchlorate to form hexaquochromium perchlorate, which was then allowed to react with potassium dioxalatochromiate according to the equation:

$$K\ [CrOx_2(H_2O)_2] + [Cr(H_2O)_6](ClO_4)_3 \rightarrow [Cr(H_2O)_6]\,[CrOx_2(H_2O)_2]\,(ClO_4)_3$$

The liquor thus prepared was aged for about 6 months at 20° to 25°C., and the quantities of cationic chromium and of oxalate associated with the cationic chromium were determined at intervals by the ion exchange technique previously reported (15). A 40-ml. portion of the liquor, containing 0.1%

TABLE I

CHANGES UNDERGONE BY THE COMPOUND $[Cr(H_2O)_6][CrOx_2(H_2O)_2]ClO_4$ DURING AGING

	Unaged	Aged 2 days	Aged 1 week	Aged 2 weeks	Aged 4 months	Aged 6 months
Mg. Cationic Cr in 40 ml.	21.07	22.67	30.31	31.55	39.59	40.66
Ratio of cationic Cr to total Cr	0.5066	0.5450	0.7285	0.7585	0.9540	0.9773
Ratio of oxalate to Cr in the cation	0.00	0.41	0.63	0.73	0.99	1.02

Cr_2O_3, was passed through a 5-g. column of Amberlite IR-4B-acetate, 8 mm. in diameter and 150 mm. long, at 40°C., to remove anionic chromium. The quantity of cationic chromium and the ratio of oxalate to cationic chromium were determined in the effluent. The results are shown in Table I.

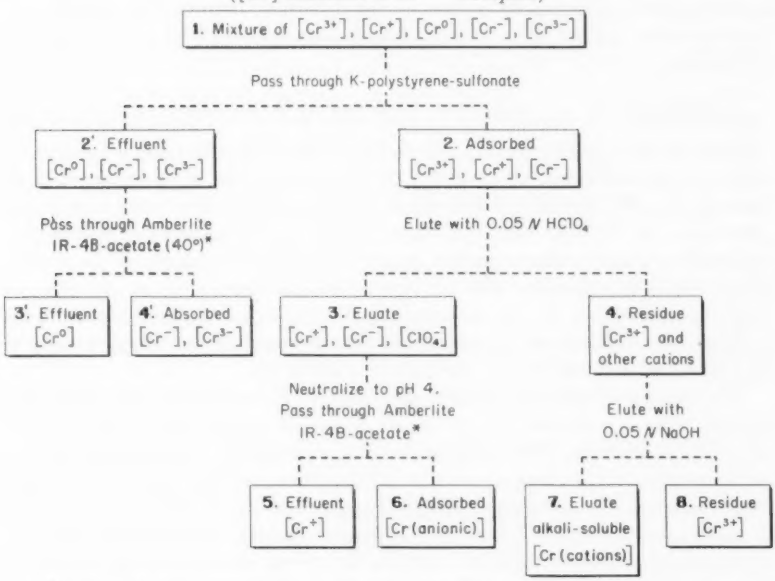
During aging, the color of the liquor changed from blue-violet to reddish violet. At the end of aging, the chromium in the effluent from Amberlite IR-4B-acetate was absorbed completely by the cationic exchanger Amberlite IR-120. We presume from these facts that part of the oxalate originally in the anionic side of the complex gradually migrated to the cation, producing a cationic complex with one positive charge:

$$[Cr(H_2O)_6]\ [CrOx_2(H_2O)_2]\ [ClO_4]_2 \xrightarrow{\text{aging}} 2[CrOx(H_2O)_4]ClO_4$$

After aging for one month, the $[CrOx(H_2O)_4]ClO_4$ was separated by the following procedure: All the cationic chromium was adsorbed on a polystyrene resin (H-form); then only the singly charged cationic complexes were eluted, using 0.05 *N* $HClO_4$. The eluate was passed through a low-cross-linked (DVB 1 – 2%), styrene-type, strongly basic anion exchanger (perchlorate form) to remove a little anionic chromium that accompanied the monopositive Cr complex. This procedure is based on an analytical method for separating chromium complexes, previously reported, which is outlined below.

PROCEDURE FOR ANALYZING A MIXTURE OF COMPLEX CHROMIUM IONS

([Cr] indicates a Cr III Complex)


1. Mixture of [Cr3+], [Cr+], [Cr0], [Cr−], [Cr3−]
Pass through K-polystyrene-sulfonate
2'. Effluent [Cr0], [Cr−], [Cr3−]
2. Adsorbed [Cr3+], [Cr+], [Cr−]
Pass through Amberlite IR-4B-acetate (40°)*
Elute with 0.05 N HClO4
3'. Effluent [Cr0]
4'. Absorbed [Cr−], [Cr3−]
3. Eluate [Cr+], [Cr−], [ClO4−]
4. Residue [Cr3+] and other cations
Neutralize to pH 4. Pass through Amberlite IR-4B-acetate*
Elute with 0.05 N NaOH
5. Effluent [Cr+]
6. Adsorbed [Cr (anionic)]
7. Eluate alkali-soluble [Cr (cations)]
8. Residue [Cr3+]

*Or strongly basic styrene-type anion exchanger (DVB 1.0–2.5%).

$[Cr^{3+}] = (4) - (7) = (1) - (2') - (3) - (7)$
Alkali-soluble [Cr(cationic)] $= (7)$
$[Cr^{+}] = (5)$
$[Cr^{0}] = (3')$
[Cr(anionic)] $= (4') + (6) = (2') - (3') + (3) - (5)$

As the resulting liquor contained $HClO_4$ besides $[CrOx(H_2O)_4]ClO_4$, free acid was determined by a conductimetric titration and neutralized exactly with KOH. The liquor was frozen several times to concentrate the chromium compound and to remove as much $KClO_4$ as possible by crystallization. The color of the final solution was purple-red, with maximum absorption bands at 419–420 and 554–560 mμ. The ratio of oxalate to Cr was 1.02.

To synthesize $K[Cr^*Ox_2(H_2O)_2]$, metallic Cr*, obtained from the Atomic Energy Research Establishment, Harwell, England, with a half life of 27.8 days, was dissolved in $HClO_4$, oxidized to chromate with H_2O_2 in KOH solution, and filtered to remove $Fe(OH)_3$ which was present as an impurity. A tenfold quantity of ordinary $K_2Cr_2O_7$ was added to the filtrate to act as a carrier. The reduction of chromate was done with oxalic acid, and radioactive trans-potassium dioxalatochromiate crystals were obtained by the usual method.

The solutions of $K[Cr^*Ox_2(H_2O)_2]$ and $[CrOx(H_2O)_4]$ ClO_4 were made to the same concentration and mixed. Precipitated $KClO_4$ was removed by centrifugation. The composition of the resulting material in solution appeared to be $[CrOx(H_2O)_4]$ $[Cr^*Ox_2(H_2O)_2]$ accompanied by a small amount of $KClO_4$.

TRANSITION OF RADIOACTIVE CHROMIUM BETWEEN COMPLEX IONS

Immediately after preparation the solution of $[CrOx(H_2O)_4]$ $[Cr^*Ox_2(H_2O)_2]$ was diluted to contain about 1% Cr_2O_3, and portions of the solution were brought to pH 2.0 and 4.0 with dilute $HClO_4$ and KOH. After storage for one week at 1°–3° C. the aged solutions were compared with the original ones with respect to the composition of the complex ions and the distribution of Cr* between the ions. The analysis of charge distribution in the complex ions was carried out by the procedure outlined above. At the same time the radioactive strength of each fraction was determined by using a Geiger-Müller counter. The results are shown in Table II.

The determinations of radioactivity were made as follows: A round filter paper, 24 mm. in diameter, was placed in the bottom of a flat-bottomed dish 25-mm. in diameter. The sides of the dish were coated with vaseline to prevent creeping. The chrome liquor was poured on the filter paper and evaporated under an infrared lamp. When the depth of liquor had fallen to about 2 mm., one drop of a 1% sucrose solution was added to prevent curling and shrinking of the paper. In this way the chromium was uniformly distributed

over the paper. Measurement of radioactivity was done at a distance of 13 mm. from the mica window of the G-M tube (G-M 131) for 30 minutes.

TABLE II

EFFECT OF AGING OF $[CrOx(H_2O)_4] \cdot [Cr^*Ox_2(H_2O)_2]$ ON PROPORTIONS OF CATIONIC AND ANIONIC CHROMIUM, AND ON DISTRIBUTION OF RADIOACTIVE CHROMIUM (Cr^*)

		Aged 7 Days	
	Unaged	at pH 2	at pH 4
Cationic Cr : mg.	18.1	17.97	19.07
" " : % of total	43.0	42.7	45.3
Anionic Cr : mg.	24.0	24.13	23.03
" " : % of total	57.0	57.3	54.7
Radioactivity of cationic fraction:			
Counts per min.	none	395±21	345±20
% of total	none	39.2±2.1	34.2±2.3
Radioactivity of anionic fraction:			
Counts per min.	1009±32	614±26	664±27
% of total	100	60.9±2.5	65.9±3.3

As shown in Table II the charge distribution between the complex ions changed hardly at all in one week's aging. However, after a week the distribution of radioactivity changed greatly. About 35% of the radioactivity was found in the cationic fraction after one week at pH 4, and 40% at pH 2. This indicates a transition of oxalate radicals from the anionic to the cationic part of the compound. Judging from this, the individual Cr atoms in the two fractions of the aged sample were not always the same ones that were present in those two fractions before aging, even though no change took place in the relative proportions of the two fractions during aging. In other words, even in such stable complexes as the oxalato-chromium compounds, and even when equilibrium has been established with respect to the ratio of cationic to anionic complexes, an interchange of coordinated acid radicals between cation and anion unexpectedly occurs. Thus an apparent equilibrium of charge distribution determined by ordinary methods does not always agree with the results of equilibrium studies by the tracer technique using ^{51}Cr.

EXAMINATION OF THE NATURE OF CHROMIUM ADSORBED BY GELATIN GELS

From the data in Table I we recognized the transition of coordinated acid residues between cationic and anionic complexes, even in the case of such a stable residue as the oxalate ion. Therefore, we felt it necessary to study the

process of adsorption of each kind of chromium by collagen in the case where various complexes coexist in the liquor. Such experiments have been made using gelatin gels in place of collagen.

Purified powdered gelatin was dissolved in hot water to make a 30% solution. This solution was divided into 3 parts which were adjusted to pH values of 3.0, 4.0, and 4.6 by adding 0.1*N* $HClO_4$ or 0.1*N* KOH, and diluted to a gelatin concentration of 25%. After these gelatin sols were held in the hot state to get rid of air bubbles, they were poured into flat dishes to a depth of 10 mm., cooled to 1°–3°C., and cut into blocks 13 x 13 x 10 mm.

The chrome liquors studied were solutions of the following 5 compounds, all containing 1% Cr_2O_3: $[Cr(H_2O)_6](ClO_4)_3$, $[CrOx(H_2O)_4]ClO_4$, $K[CrOx_2(H_2O)_2]$, $K_3[CrOx_3]$, and $[CrOx(H_2O)_4][Cr^*Ox_2(H_2O)_2]$ used immediately after synthesis, or the same compound made with ordinary chromium throughout. Portions of each kind of liquor were adjusted to pH values of 3.0, 4.0, and 4.6.

Ten blocks of gelatin gel having the same pH as the chrome liquor were soaked in each chrome solution for one week at 1°–3°C. Each set of 10 blocks was then rinsed with 50 ml. of water and stored at 5°–7°C. Since gelatin gels retain far more unadsorbed chromium than skin does, 3 blocks out of each set of 10 were washed and then analyzed to determine the net quantity of combined chromium. The 3 blocks were put into a test tube 100 mm. long x 25 mm. in diameter and washed with 1500 ml. of running distilled water flowing at 1.2–1.5 ml. per min., at 5°–7°C. The washed gels were dried and analyzed for chromium (by the Na_2O_2 fusion method) and for nitrogen.

The quantities of chromium retained by the gels before and after washing are shown in Table III. It is evident that the quantities of chromium fixed after washing are scarcely related to pH value (in the range 3.0–4.6) in the case of the anionic chromium compounds (potassium dioxalato- and potassium trioxalatochromiate), while combination of cationic chromium increases markedly with pH value. The mixed compound, $[CrOx(H_2O)_4][CrOx_2(H_2O)_2]$, shows almost the same tendency as the purely cationic compounds. From this it might be concluded that only the cationic portion of this compound acts upon gelatin gels.

In order to find out the significance of the coexistence of the chromium complex anion, the same chroming experiment was repeated with the labelled compound, $[CrOx(H_2O)_4][Cr^*Ox_2(H_2O)_2]$, prepared from radioactive Cr^* as already described. After treating the gelatin blocks in liquors of the same pH values as before, they were washed as before, then analyzed, and the strength of the remaining radioactivity was measured. All the determinations of radioactivity were performed under conditions as nearly alike as possible to avoid the errors which were chiefly caused by self-absorption. The results are given in Table IV.

TABLE III

QUANTITIES OF Cr_2O_3 ABSORBED BY GELATIN GELS

Kind of Chrome Liquor	Before Washing			After Washing		
	pH 3.0	pH 4.0	pH 4.6	pH 3.0	pH 4.0	pH 4.6
$[Cr(H_2O_6)\text{-}](ClO_4)_3$	3.63%	3.97%	5.99%	1.00%	2.67%	5.73%
$[CrOx(H_2O)_4]ClO_4$	5.73	5.11	5.63	1.96	3.28	5.22
$K[CrOx_2(H_2O)_2]$	6.35	5.47	5.23	2.07	2.48	2.02
$K_3[CrOx_3]$	6.89	7.29	6.52	1.14	1.11	0.27
$[CrOx(H_2O)_4][CrOx_2(H_2O)_2]$	5.96	5.90	6.12	2.19	3.44	4.62

TABLE IV

ABSORPTION OF CHROMIUM FROM THE ANIONIC PART OF RADIOACTIVE $[CrOx(H_2O)_4][Cr^*Ox_2(H_2O)_2]$ BY GELATIN GELS (AFTER WASHING)

pH Value	Total Cr_2O_3 Absorbed (mg.)	Isotopic Activity (30 min. counts)	Radioactive * Cr (mg.)	Percentage of total Cr_2O_3 absorbed that was anionic initially
3.0	32.24	1465 ± 50	29.8 ± 2.1	92.5 ± 6.6
4.0	38.28	1444 ± 50	29.4 ± 2.1	76.5 ± 5.5
4.6	59.13	1718 ± 54	35.0 ± 2.3	59.2 ± 3.8

*A count of 1232 ± 48 in 30 minutes for $K[Cr^*Ox_2(H_2O)_2]$ is equivalent to 25.11 mg. Cr_2O_3.

Table IV shows that the content of anionic chromium—or at least the chromium that was anionic originally—was more than 90% of the total chromium in the gel at pH 3.0, about 75% at pH 4.0, and about 60% at pH 4.6. These percentages are much too high to be explained as being caused by transition of anionic to cationic chromium before acting on the gels. These results are not in agreement with the conclusion, drawn from the quantities of chromium fixed at the different pH values, that only the cationic group of $[CrOx(H_2O)_4][CrOx_2(H_2O)_2]$ was fixed by the gel.

PHYSICAL NATURE OF THE CHROMED GELS

Physical measurements were also made on the unwashed gelatin blocks and compared with nonchromed gels. *Hardness* was measured by adding weights to a fine, stainless steel rod, 200 mm. long with a 2-mm. head, resting on the block, until a sudden intrusion of the rod into the gel took place. The added weight was taken as a measure of hardness. *Strain in compression* was measured by placing a 1000-g. weight on a thin, stainless steel plate resting on the block and measuring the thickness of the block before and

TABLE V

RESULTS OF PHYSICAL TESTS ON CHROMED, UNWASHED GELATIN GELS

Kind of Chrome Liquor	Mean Values and 95% Confidence Limits					
	Hardness*			Strain in Compression†		
	pH 3.0	pH 4.0	pH 4.6	pH 3.0	pH 4.0	pH 4.6
$[Cr(H_2O)_6](ClO_4)_3$	128 ± 50	1018 ± 123	2072 ± 236	41.4 ± 1.8	14.7 ± 1.0	7.9 ± 1.2
$[CrOx(H_2O)_4]ClO_4$	169 ± 52	713 ± 110	1146 ± 120	41.5 ± 1.3	16.9 ± 1.7	9.6 ± 1.5
$K[CrOx_2(H_2O)_2]$	68 ± 14	303 ± 89	555 ± 131	43.5 ± 2.7	27.6 ± 0.8	18.0 ± 1.7
$K_3[CrOx_3]$	46 ± 5	49 ± 6	46 ± 4	46.7 ± 2.7	42.6 ± 3.1	41.3 ± 1.9
$[CrOx(H_2O)_4][CrOx_2(H_2O_2)]$	148 ± 41	552 ± 77	1237 ± 92	40.7 ± 3.1	18.3 ± 2.6	10.1 ± 1.5
Blank (unchromed)	93 ± 6	143 ± 25	172 ± 16	34.1 ± 2.1	28.7 ± 1.1	25.2 ± 2.5

*Penetration load in grams.

†$(t_1 - t_2)/t_1$ where t_1 is initial thickness and t_2 is thickness under a compressive force of 1000 g.

TABLE VI

BEHAVIOR OF CHROMED, UNWASHED GELATIN GELS ON HEATING IN WATER

	pH	$[Cr(H_2O)_6](ClO_4)_3$	$[CrOx(H_2O)_4]ClO_4$	$[CrOx(H_2O)_4]$-$[CrOx_2(H_2O)_2]$	$K[CrOx_2(H_2O)_4]$	$K_3[CrOx_3]$
Melting point or time of boiling	3.0	Resists 100° for 5 min.	Resists 100° for 5 min.	Dissolves at 100° in 3 min.	Dissolves at 36° – 37°	Dissolves at 23 °– 25°
	4.0	same	same	Resists 100° for 5 min.	Dissolves at 100°, 4 min.	Dissolves at 30° – 31°
	4.6	same	same	same	Resists 100° for 5 min.	Dissolves at 32° – 33°
% dissolved after boiling	3.0	0.3	38	100	100	100
	4.0	none	0.5	2	100	100
	4.6	none	none	none	4	100
Brittleness	3.0	+	—			
	4.0	++++	+++	++		
	4.6	++++	+++	++	—	
Degree of softening	3.0	++	++++			
	4.0	+	++	+++		
	4.6	+	++	++	+++	
Degree of swelling	3.0	30				
	4.0	20	10	none		
	4.6	21	10	none	20	

after weighting. The percentage reduction in thickness (reduction in thickness / initial thickness) was regarded as "strain in compression." Both these measurements were done in a cool chamber at 6° ± 1°C. Each measurement was done on 6 blocks. In addition, the temperature at which the blocks dissolved in hot water was determined, and for those blocks that did not dissolve at 100°C., the states of the gels after heating were observed.

The results of the physical tests and melting point determinations (Tables V and VI) again show that the nature of the chromed gels obtained with $[CrOx(H_2O)_4][CrOx_2(H_2O)_2]$ is almost the same as that of the gels obtained with $[CrOx(H_2O)_4]\ ClO_4$, and very different from that of the gels obtained with $K[CrOx_2(H_2O)_2]$. These facts agree with the amounts of chromium absorbed (Table III).

DISCUSSION

Gustavson (17–19) has already asserted the importance of noncationic chromium in chrome tanning and has stated that the initial fixation of the chromium complex to collagen might be noncationic; however, cationic complexes might be formed gradually and react with the carboxyl groups of collagen. This conversion may occur in the tanning process itself or during subsequent washing. Gustavson also explained the importance of the charge of the complex with regard to access to the reactive groups of the protein, the sphere of activity of the latter being limited to a few Angstrom units.

In previously published work such transitions have been noted only in the case of unstable anionic complexes, but according to our experiments even such stable complexes as oxalatochromium compounds can show an interchange of coordinated acid residues between coexisting cationic and anionic complexes. These exchanges seem to happen in the presence of collagen. Chrome tanning is always performed at pH values on the acid side of the isoelectric point of collagen. Therefore, anionic chromium can combine, at least in part, with basic groups of the protein. But it is well known that simple electrovalent combination does not produce a stable leather such as is produced in chrome tanning.

In our experiments with gelatin, anionic chromium, unexpectedly, was retained in large quantity after washing in the case of gels tanned with the mixed cationic-anionic chromium compound, while when merely anionic chromium was used, the absorbed chromium was largely removed by washing. On the other hand, the physical nature of the gels tanned with $[CrOx(H_2O)_4][CrOx_2(H_2O)_2]$ is almost the same as that of gels tanned with wholly cationic compounds.

From these results it is assumed that in the tanning process anionic chromium may be slightly fixed to the basic groups of collagen, by electrovalent bonds at first, then converted to cationic chromium while fixed to collagen, while an equivalent amount of anionic chromium is formed in the liquor.

Therefore no accurate measurement can be made of changes in the charge distribution in the liquor. As a secondary reaction the newly formed cationic chromium may coordinate with the carboxyl radicals of collagen, producing a stable chrome leather.

As anionic chromium is not appreciably olated, it may be able to penetrate more easily into the inside structure of collagen.

Of course, a stable anionic complex has the capacity to combine with hide without change of charge, producing a less stable leather, as in the case of typical anionic chrome tannage. But under the condition of coexistence of both anionic and cationic complexes a part of the anionic complexes may have a facilitating effect on the formation of the chromium-protein compound, regardless of the initial stability of the complex.

SUMMARY

To study the significance of anionic chromium in chrome tanning the authors synthesized the compound $[CrOx(H_2O)_4][Cr^*Ox_2(H_2O)_2]$, in which the anionic Cr was labelled with radioactive $^{51}Cr^*$. The radioactivity of the cationic chromium in this compound was measured after aging for one week. The distribution of charges and the distribution of radioactivity did not wholly agree. Practically no change took place in the ratio of cationic to anionic chromium, but a considerable part of the radioactivity was transferred to the cationic side of the complex.

The quantities of chromium absorbed by gelatin gels and the physical properties of the gels were measured after treating them with various chromium complexes, including $[CrOx(H_2O)_4][Cr^*Ox_2)(H_2O)_2]$. In the gel tanned with this compound both the amount of chromium combined and the physical properties of the gel were similar to the results obtained with the purely cationic chromium compound $[CrOx(H_2O)_4]ClO_4$. However, radioactivity measurements showed that 60 to 90% of the chromium combined in the gel originated in the anionic part of the $[CrOx(H_2O)][Cr^*Ox_2(H_2O)_2]$.

From these inconsistent findings we conclude that the presence of anionic complexes may have an accelerating effect in chrome tanning. Possible reasons for this effect are discussed.

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A pair of gloves of Queen Elizabeth may still be seen in the Bodleian Library at Oxford. They are reported to have been worn by her on the occasion of her visit to the University in 1566. These are close upon 16 ins. long, and are finished at the gauntlet with a 2 in. fringe of gold thread. The gloves themselves are of exceedingly fine white leather, beautifully embroidered with a scroll-work of gold thread which covers the gauntlet and is continued round the base of the thumb. The size of these gloves in remarkable, the middle finger being close upon 5 ins. long, the thumb quite 5 ins. and the width at the palm 3½ ins. —*Gloves and the Glove Trade*. B. Eldred Ellis. London: Sir Isaac Pitman & Sons, Ltd., 1921.

MEXICAN TANNERS MAKING QUALITY LEATHERS; TO SEND STUDENTS TO NEXT HIDE TRAINING COURSE

"Mexican tanneries are producing quality leather," according to a report of Merle A. Delph, President of M. A. Delph Co., Inc., Indianapolis, Ind., following a visit he made to Mexican tanneries upon invitation of members of the Mexican tanning industry. "This leather is being produced in high colors and it is very appealing," Mr. Delph said. "Certainly the art of tanning has come a long way in Mexico in recent years. That country is now producing greatly improved leathers . . . . upper leathers . . . . particularly. They are outstanding. I saw some real nice red leathers. They go in for red in Mexico. I also witnessed the making of some splendid white leather. Most of this leather is being produced for home consumption or for export other than to the United States."
— *N H A Bulletin*, April 24, 1957.

COMPLEX EQUILIBRIA IN CHROME TANNING*

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ABSTRACT

Basic chromium sulfate solutions containing masking agents were adjusted to various pH values by small additions of potassium hydroxide and hydrochloric acid. After aging, the composition of the complexes in the solution was investigated by means of ion exchange techniques. From the data obtained, determination was made of the effect at various pH values of the ionization of the weak organic acids and basicity. In Part II of this investigation, chrome-tanned hide powder was placed in water containing masking salts and adjusted to various pH values for 30 days by the addition of potassium hydroxide and hydrochloric acid as needed. From the analysis of the chrome liquor the detanning effects of various masking agents at different pH values were obtained. Through a correlation of the complex equilibria data obtained in these two investigations an explanation for the effects of masking agents and pH variations observed in practical chrome tanning is proposed.

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PART I

INTRODUCTION

The introduction of the concepts of Alfred Werner to the field of leather chemistry by Stiasny (1), Wilson (2), Thomas (3), and Gustavson (4) in the early part of the present century marked the beginning of our understanding of chromium complexes and their relation to tanning processes. Using techniques such as precipitation points, pH values, and thermal stability, Stiasny investigated the ability of various anions to enter into the chromium complexes, thereby displacing water molecules or other ions.

Stiasny postulated that the ability to form complexes with chromium varied with the anion involved and arranged the anions of interest in practical tanning in a series of increasing penetrating power (nitrate, chloride, sulfate, formate, acetate, sulfite, and oxalate). Since the time of Stiasny's work the subject of basic chromium salts has received the attention of many investi-

*Presented at the Fifty-third Annual Meeting, Lake Placid, N. Y., June 2–5, 1957. The discussion will be published in October.

gators employing many different techniques. These include pH titrations, diffusion methods, ionic sulfate determinations, conductivity, spectrophotometry, polarography, and other techniques. Use of absorption methods has led to interesting results in the hands of several investigators. Gustavson (3), in 1924, was the first to apply absorption methods to the study of chromium complexes by the use of permutite-type absorbers. Later these techniques were refined by Gustavson (5) and other workers (6, 7, 8) after the invention of exchange resins. The ion exchange resins, by means of their specific absorbing properties, can be applied for the separation of the cationic, nonionic, and anionic complexes as well as for chemical analysis of these complexes by both direct and indirect methods.

The same general technique is followed in this work that was originally used by Theis and his co-workers in previous studies (9). The resin* is saturated with the hydrogen ion by washing with a solution of strong acid. Upon addition of the solution containing cationic chromium complexes the complex reacts with the resin according to the following equation:

$$R - H + [Cr\ A_4\ B_2]^+ \rightleftarrows R - [Cr\ A_4\ B_2] + H^+$$

where $[Cr\ A_4B_2]^+$ is a typical cationic complex containing 4 neutral and negative molecules or ions. Upon treatment with a strong acid the reaction is reversed, and the complex is stripped from the resin. By analyzing the original solution and the strongly acid effluent solution containing the cationic complexes, the composition of the complexes absorbed can be determined.

There are two inaccuracies which result from this technique. First, the absorption of the cationic complexes and the release of hydrogen ions by the resins change the pH of the solution, which immediately upsets the equilibria of the complex ions. Second, there may be some errors resulting from the coabsorption of small quantities of nonionic and anionic materials. These errors may decrease the validity of quantitative conclusions concerning the composition of the complexes; however, the qualitative effects relative to the penetration of one ion or the other in a cationic complex are accurate within reason and allow logical conclusions to be drawn.

PROCEDURE

The liquor used for this study was a concentrated (15% Cr_2O_3) 33% basic chromium sulfate, prepared by sulfur dioxide reduction of sodium dichromate. The various complexing materials used were recrystallized sodium salts of analytical grade.

The solutions studied all contained 5% KCl, 1.25% Cr_2O_3, and KOH or HCl as needed to adjust the pH. In mixing the solutions the concentrated

*Ionac resin C-200 (activated), American Cyanamid Company.

chromium liquor was added to a solution containing the potassium chloride. A solution containing the sodium salt (formate, acetate, etc.) to give the concentration desired was then added, and the entire mixture was diluted quantitatively to yield a final concentration of 1.25% Cr_2O_3 and 5% KCl. The solution was then divided into 8 portions of about 500 ml. each. These 8 identical solutions were adjusted to pH values from 2.0 to 5.0 by the addition of KOH solution or HCl as needed. The pH values of the solutions were readjusted every 48 hours for 30 days, thus keeping the pH near the desired value.

A static technique in treatment of resin and solution was used. One-hundred-gram portions of the wet resin (about 75 ml. of the resin-water slurry) were placed in 125-ml. Erlenmeyer flasks, and the excess water was decanted. Twenty-five-ml. samples of the chrome solutions were pipetted into the flasks, and the flasks were shaken intermittently for 30 minutes, after which the resin and solution were poured into a glass tube stoppered at the bottom with glass wool. The resin was washed clear of unabsorbed substances with 150 ml. of distilled water. The combination filtrate and wash was diluted to 250 ml. for analysis for chromium, sulfate, and the organic anion.

The resin was then removed from the tube and placed in 6 *N* sulfuric acid for 48 hours, after which the resin was again placed in the tube and washed clear with 6 *N* sulfuric acid. This procedure did not in all cases remove 100% of the absorbed chromium, but the procedure was accepted as standard since much larger volumes of acid would be impractical. The resulting solution was diluted to 250 ml. and analyzed for chromium and the various organic anions. Sulfate in the complex was taken as the difference between the amount in the original solution and the amount found in the water-wash solution. The analysis of the water-wash and the acid-wash solutions was by standard techniques: The chromium determination was by oxidation with perchloric acid and titration with ferrous sulfate; sulfate, by precipitation with barium sulfate; and the organic acids, by dichromate oxidation except that acetate was determined by distillation as acetic acid and subsequent titration with potassium hydroxide solution.

Unmasked liquors.—In order later to interpret data obtained on masked solutions, 33% basic chromium sulfate without added masking agents was investigated in the manner just described. Precipitation took place slowly at the higher pH values (4.5 and 5), but the other solutions remained clear. At the end of 30 days the clear solutions were treated with the exchange resins and analyzed in the manner described above. The results of these analyses are shown in Table I and Figure 1. The liquor remains predominantly cationic over the entire pH range studied. There is a gradual decrease in the sulfate acidity of the complex with increasing pH values which may

TABLE I

EFFECT OF pH VALUE UPON THE CATIONIC COMPLEXES OF 33% BASIC CHROMIUM SULFATE

Sample	pH	% Cationic	Sulfate Acidity
1	2.0	74.5	26.6
2	2.5	79.1	23.2
3	3.0	83.0	20.4
4	3.3	87.5	21.7
5	3.6	87.7	19.1
6	4.0	72.6	17.8

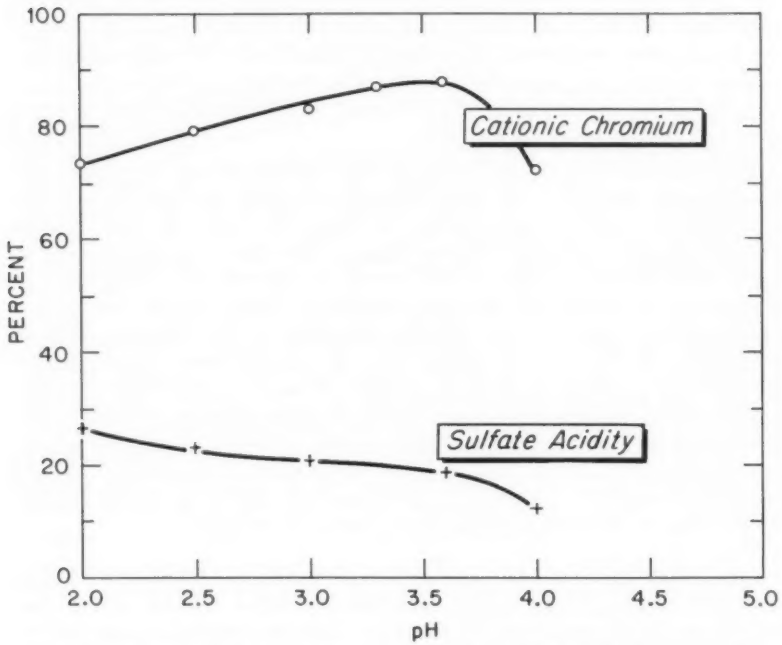

FIGURE 1.—The effect of pH upon the cationic complexes of 33% basic chromium sulfate.

be attributed to the entering of hydroxyl groups into the complex at higher pH values which results in the displacement of some of the sulfate from the complex. With an increase in pH and basicity there is observed an increase

in the amount of chromium present as cationic complexes. This is due in part to the decrease in the sulfate acidity of the complexes at higher pH values.

With an increase in pH and basicity in a chrome liquor there is also an increase in the size of the complexes due to olation. If the olation takes place without the displacement of a charged group from the complex, the net charge on the resulting aggregate is the sum of the charges of the complex ions involved. If one of these components is nonionic and one cationic, a net cationic charge results. This, by the method used in this experiment, results in an apparent increase in the cationic nature of the solution. The acid solution containing the cationic complexes gave only a slight turbidity upon the addition of silver nitrate, indicating negligible coordination of the chloride ion into the complex. The decrease in percentage of cationic chromium at the highest pH value is of questionable significance because of the partial precipitation that occurred.

Formate additions.—The complexes formed by the addition of sodium formate to a solution of basic chromium sulfate at various pH values were investigated in the same manner. These solutions were handled like the previous series except that the solutions were 0.2 *M* with respect to sodium formate. The resulting data are given in Table II and Figure 2. From the inspection of this data it can be seen that the formate replaces the sulfate in the complex. This replacement takes place over the entire pH range studied but to a greater extent at pH values above 3. The fixation of relatively large quantities of formate at the lower pH values where there is little ionization of the formic acid can probably be attributed to the equilibrium between the chromium and the formate ion being the dominant effect rather than the ionization of the formic acid. At pH values above 3.5 essentially all of the formate is present in the ionized state (ionization constant 2.14×10^{-4}), therefore favoring further coordination. Since the pH adjustments were

TABLE II

EFFECT OF pH VALUE UPON THE CATIONIC COMPLEXES OF 33% BASIC CHROMIUM SULFATE IN 0.2 *M* SODIUM FORMATE

Sample	pH	% Cationic	Sulfate Acidity	Formate Acidity	Total Acidity
1	2.0	75.4	13.5	17.8	31.3
2	2.5	81.8	12.8	16.2	29.0
3	3.0	82.7	10.2	20.1	30.3
4	3.3	88.3	7.8	23.3	31.1
5	3.6	87.2	7.4	26.5	33.9
6	4.0	90.0	8.8	24.0	32.8
7	4.5	78.4	6.1	27.9	34.0

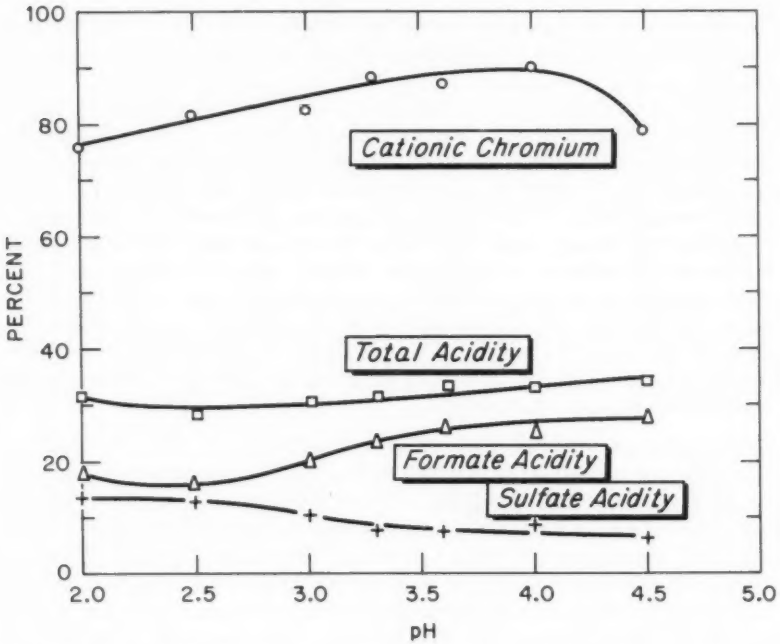

FIGURE 2.—The effect of pH upon the cationic complexes of 33% basic chromium sulfate in the presence of sodium formate.

made by the addition of acid and alkali, the removal of formate ion through the complex formation does not affect the further ionization of the formic acid. Two factors are evidently involved here: one, the equilibrium between the formate ion and the chromium; the other, the ionization of formic acid at various pH values. The general rise in the cationic complexes can be attributed to olation as in the previous series.

Acetate additions.—Acetate has a greater tendency than formate to form complexes with chromium. A series of liquors similar to that used for sodium formate studies was made using sodium acetate. The solutions were treated in the same manner and analyzed by means of the exchange resin techniques outlined above. The data obtained in this series are presented in Table III and Figure 3. With increased pH values there is an increased formation of chromium acetate complexes with the displacement of sulfate. This occurs in a manner similar to the sodium formate solutions but to a greater extent. Here again we observe that even at the lower pH values a relatively high fixation of acetate in the chrome complex occurs. Acetic acid,

TABLE III

EFFECT OF pH VALUE UPON THE CATIONIC COMPLEXES OF 33% BASIC CHROMIUM SULFATE IN 0.2 *M* SODIUM ACETATE

Sample	pH	% Cationic	Sulfate Acidity	Acetate Acidity	Total Acidity
1	2.0	76.4	14.6	16.6	31.2
2	2.5	75.2	12.3	22.9	35.2
3	3.0	74.8	8.5	23.6	32.1
4	3.3	73.9	3.9	25.7	29.6
5	3.6	75.5	4.9	26.1	31.0
6	4.0	78.1	3.0	28.6	31.6
7	4.5	78.6	3.0	28.9	31.9
8	5.0	80.3	1.6	34.7	36.3

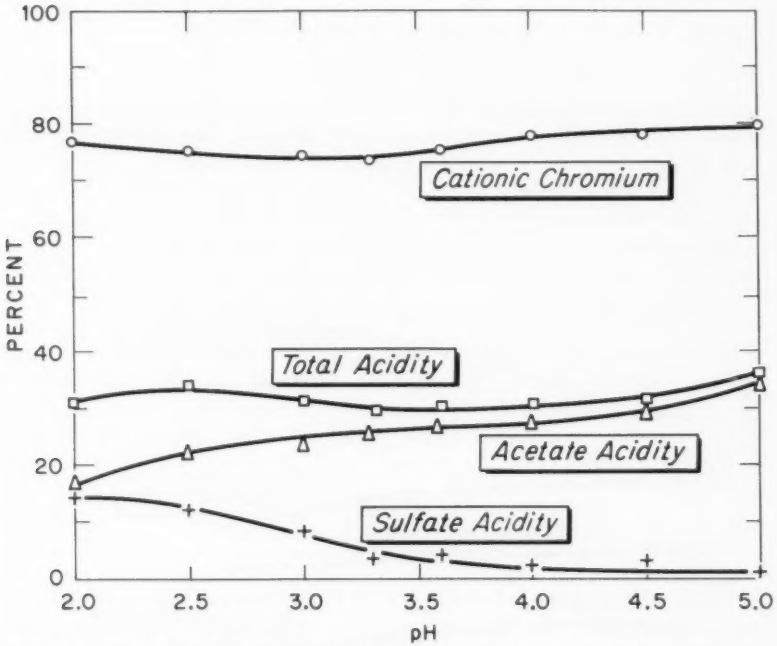

FIGURE 3.—The effect of pH upon the cationic complexes of 33% basic chromium sulfate in the presence of sodium acetate.

with an ionization constant of 1.8×10^{-5}, becomes ionized at higher pH values than formic acid, resulting in an increase in acetate ion concentration at the higher pH value studied. Quantitative interpretation of the data in terms

of ionization constants would probably not be valid because of the complicated nature of the system. The percent of cationic complexes remains approximately constant, indicating that olation in this case may have taken place to a somewhat lesser extent than in the previous two series.

Oxalate additions.—It is well known that oxalate will form very stable complexes with chromium. The investigation conducted on oxalate complexes was made in the same manner as the previous two sets. The solutions

TABLE IV

EFFECT OF pH VALUE UPON THE CATIONIC COMPLEXES OF 33% BASIC CHROMIUM SULFATE IN 0.1 *M* SODIUM OXALATE

Sample	pH	% Cationic	Sulfate Acidity	Oxalate Acidity	Total Acidity
1	2.0	49.8	12.6	26.2	38.8
2	2.5	53.4	17.5	25.7	43.2
3	3.0	60.7	12.2	24.5	36.7
4	3.3	61.7	11.4	25.1	36.5
5	3.6	59.5	10.6	23.2	33.8
6	4.0	54.2	8.1	23.5	21.6

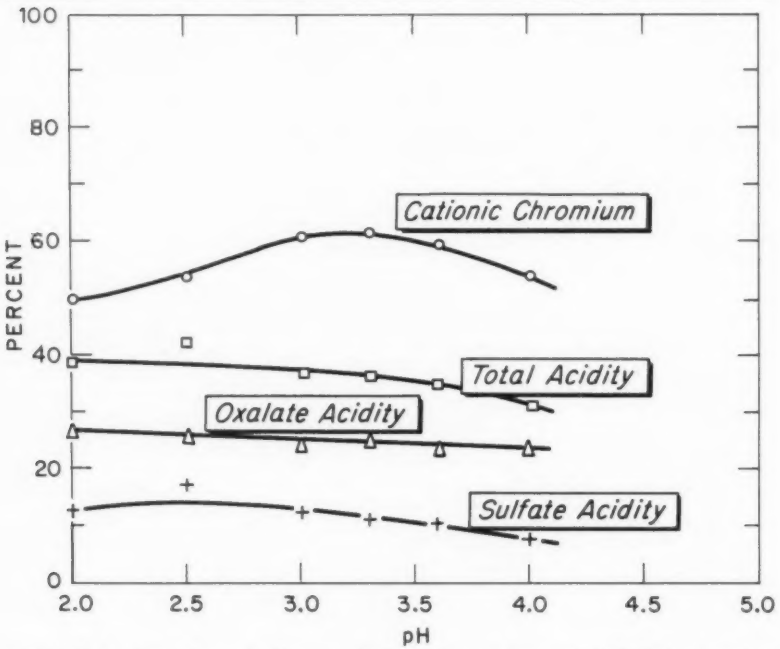

FIGURE 4.—The effect of pH upon the cationic complexes of 33% basic chromium sulfate in the presence of sodium oxalate.

were made 0.1 *M* in sodium oxalate rather than 0.2 *M* because the oxalate is a dibasic acid. The data obtained from this series are given in Table IV and Figure 4. The great tendency for the formation of chromium oxalate complexes is evidenced by the uniformly high oxalate acidity throughout the pH range. There is a decrease in the sulfate acidity with increasing pH. These two factors are related. The oxalate, having an ionization constant of 3.8×10^{-2}, is a relatively strong acid, and therefore its ionization is not as greatly affected over the pH range studied as the previous two acids. The oxalate and the sulfate must, therefore, compete with the hydroxyl ion for coordinate position. With increasing pH values the hydroxyl ion gains the advantage, and there is a displacement of the oxalate and sulfate resulting in a decrease in the total acidity.

The increase in cationic complexes can be attributed to olation effects, and its ultimate decrease would be due to the negative charges added by the hydroxyl ions.

SUMMARY

The investigation of the complex formation of various masked chrome liquors at different pH values has been conducted under different pH conditions using ion exchange resin techniques. The data have been presented to show the composition of the resulting cationic complexes. In all cases the organic anion was found to replace the sulfate over the entire pH range studied. In the case of weak organic acids complex formation was favored at pH values where greater ionization of the weak acid occurred. Degree of penetration of weak organic acids into chromium complexes is related more to the nature of the organic acid than to its degree of ionization. Penetration of oxalate into the chrome complex is relatively unaffected by pH changes over the range studied. At higher pH values the increased penetration of hydroxyl groups into the complex can, through olation, cause an apparent increase in the cationic nature of the chromium complexes.

PART II

INTRODUCTION

In Part I the effect of various masking agents on complex formation at various pH values was investigated. In this part the formation of these complex ions in the presence of hide substance will be considered.

One concept has appeared almost universally among the later theories of chrome tannage: the concept of the formation of a chromium protein complex through the free carboxyl ions of the protein. For the sake of simplicity we shall consider chrome tanning to be the reaction of the carboxyl ions of the protein in the formation of a complex. We may, therefore, consider

chrome tannage to be simply complex formation similar to complex formation with masking agents. This is not to imply that the coordination of the carboxyl ions of the protein is the only significant factor to be considered in chrome tanning, but it is believed to be one of the most significant and worthy of our consideration.

If a reaction has taken place between the chromium and the protein, the chromium is no longer in solution. The chromium-protein complex can be easily removed as a tanned hide powder rather than by resorting to the use of exchange resins as is necessary with soluble complex ions. We should be able to approach chromium-protein complex equilibria at various pH values from either direction; that is, we can use for our studies either a tanning or a detanning effect. In this investigation a detanning effect was used.

From a practical standpoint we know that substances forming stable complexes when used as masking agents in chrome tanning reduce the fixation of the chromium in the leather. This can be explained best by assuming that the complexes have decreased tanning properties because they are so stable as to prevent the penetration of the protein carboxyl ion into the complex. Thus we can consider the hide substance itself as a complexing agent. The hide substance can replace those substances having less coordinating power than the hide protein and be replaced by those materials which form still more stable complexes. This may be an oversimplified explanation in that several groups may be coordinated simultaneously, with possible effects on one another. We would expect also that the degree of complex formation between the chromium and the hide substance would depend upon the reactive groups of the protein available at that particular pH value. The tendency of the hide protein, being a weak organic acid, toward complex formation should be a function of pH similar to that observed in the exchange resin studies of sodium formate and sodium acetate given in the first part of this paper. Through study of the relationship between complex formation of chromium with hide substance and masking agents, we should be able to observe the relative stability of the chromium-protein complex under various conditions.

PROCEDURE

One hundred grams of American Standard Hide Powder were tanned for 2 weeks in 2000 ml. of solution containing 5% KCl and 1% Cr_2O_3 (a sulfur dioxide–reduced chrome liquor, 33% basic) without adjustment of pH. Final pH of this tannage was 3.3. After tanning, the hide powder was filtered on a Buchner funnel, weighed quickly, and then placed in a stoppered jar for future use.

Nine bottles were prepared, each containing 90 ml. of 5% KCl solution. Portions of moist tanned hide powder corresponding to 4.5 g. of the original hide powder were weighed and placed in these solutions. These solutions

TABLE V

EFFECT OF pH WITHOUT ADDED MASKING AGENTS

Desired pH	Final pH	% Cr_2O_3 in liquor	% SO_3 in liquor	Cr fixed*	SO_4 fixed†	SO_4/Cr fixed‡	Cr ratio**
2.0	2.2	0.0240	0.1325	2.350	0.535	0.228	2.36
2.5	2.6	0.0188	0.1312	2.400	0.592	0.225	3.00
3.0	3.1	0.0099	0.1295	2.484	0.555	0.223	6.34
3.3	3.4	0.0082	0.1330	2.505	0.532	0.212	7.76
3.6	3.55	0.0064	0.1328	2.515	0.532	0.211	10.05
4.0	3.75	0.0053	0.1321	2.516	0.538	0.214	12.05
4.5	4.1	0.0047	0.1269	2.540	0.569	0.224	13.7
5.0	4.3	0.0040	0.1392	2.550	0.490	0.192	16.2
6.0	4.5	0.0012	0.1405	2.520	0.485	0.187	56.6

*Meq. Cr fixed per gram hide substance.
†Meq. SO_4 fixed per gram hide substance.
‡Meq. SO_4 fixed divided by meq. Cr fixed.
**Ratio of meq. Cr fixed per gram hide substance to meq. Cr per ml.

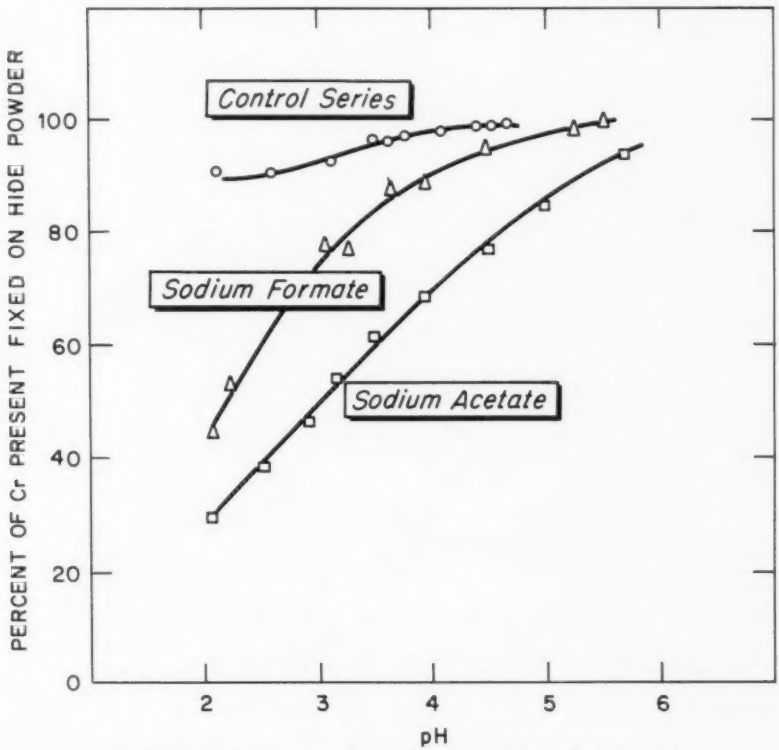

FIGURE 5.—The percent of total Cr present fixed by hide powder.

TABLE VI

SODIUM FORMATE SERIES

(Solution 0.1 M in Sodium Formate)

Desired pH	Final pH	% Cr_2O_3 in liquor	% SO_3 in liquor	Cr fixed*	SO_4 fixed†	SO_4/Cr fixed‡	Cr ratio**
2.0	2.03	.1470	.1650	1.148	.325	.283	.169
2.5	2.23	.1260	.1648	1.378	.327	.237	.238
3.0	3.08	.6020	.1722	2.002	.278	.139	.779
3.3	3.28	.0623	.1740	1.980	.268	.135	.742
3.6	3.65	.0340	.1782	2.260	.218	.0966	1.55
4.0	3.93	.0318	.1832	2.280	.208	.0915	1.70
4.5	4.48	.0139	.1848	2.455	.200	.0815	4.21
5.0	5.08	.0033	.1820	2.560	.215	.0840	18.5
6.0	5.48	.0044	.1920	2.575	.1525	.0590	13.8

*Meq. Cr fixed per gram hide substance.
†Meq. SO_4 fixed per gram hide substance.
‡Meq. SO_4 fixed divided by meq. Cr fixed.
**Ratio of meq. Cr fixed per gram hide substance to meq. Cr per ml.

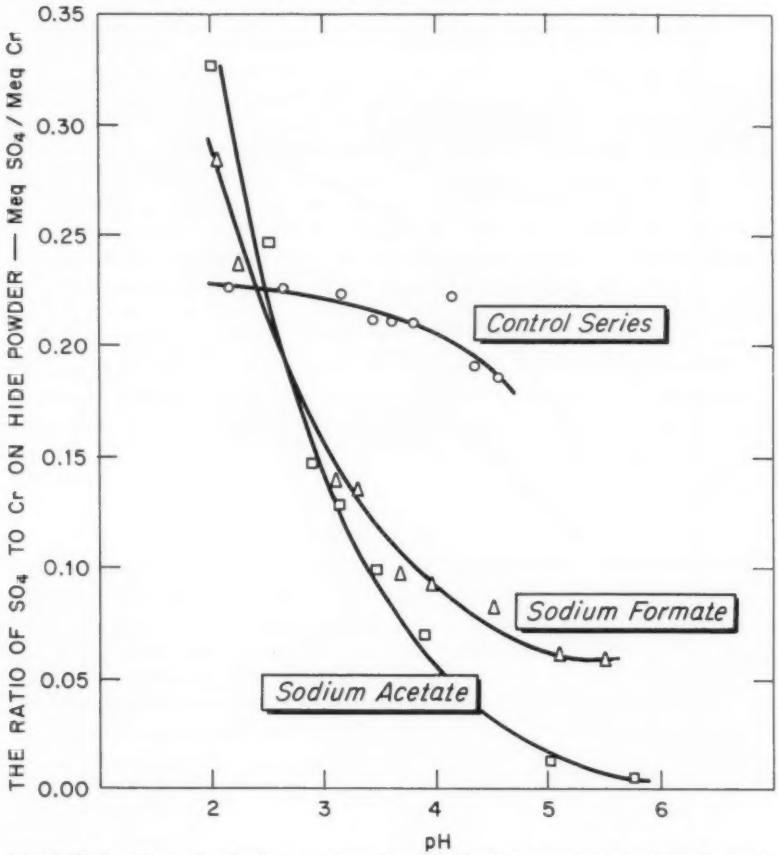

FIGURE 6.—The ratio of sulfate to chromium fixed by hide powder (Meq SO_4/Meq Cr).

TABLE VII

SODIUM ACETATE SERIES
(*Solution* 0.1 *M to Sodium Acetate*)

Desired pH	Final pH	% Cr_2O_3 in liquor	% SO_3 in liquor	Cr fixed*	SO_4 fixed†	SO_4/Cr fixed‡	Cr ratio**
2.0	2.0	.2038	.1950	.843	.275	.326	.104
2.5	2.50	.1780	.200	1.102	.248	.247	.158
3.0	2.88	.1543	.2075	1.332	.197	.148	.220
3.3	3.15	.1310	.2070	1.568	.200	.128	.305
3.6	3.45	.1104	.2185	1.770	.125	.071	.408
4.0	3.87	.0908	.2170	1.960	.137	.070	.551
4.5	4.47	.0675	.2122	2.190	.167	.076	.826
5.0	5.0	.0454	.2340	2.405	.025	.010	1.35
6.0	5.75	.0195	.2360	2.66	.015	.0056	3.48

*Meq. Cr fixed per gram hide substance.
†Meq. SO_4 fixed per gram hide substance.
‡Meq. SO_4 fixed divided by meq. Cr fixed.
**Ratio of meq. Cr fixed per gram hide substance to meq. Cr per ml.

were then adjusted to the desired pH values. The bottles were shaken in tumbling fashion for 30 days with daily adjustment for pH by the addition of potassium hydroxide or hydrochloric acid as needed. At the end of this time the hide powder was removed on a Buchner funnel, and the liquor was analyzed. Since the tanned hide powder used contained a known amount of chromium, sulfate, hide substance, and water, the amount of chromium and sulfate fixed by the hide powder could be calculated from the liquor data. A correction was applied for the dilution effects.

The above procedure was repeated using solutions which were 0.1 *M* with respect to sodium formate in one series and 0.1 *M* with respect to sodium acetate in another series. These data are given in Tables V through VII and Figures 5 through 7.

The effect of pH without added masking agents.—In the pH series without additional masking salt it is apparent that over the entire pH range there is a uniformly high fixation of the chromium by the hide powder. Increasing pH values result in only a slight decrease in the ratio between the sulfate fixed and the chromium fixed by the hide powder. The lack of loss of chromium by the hide powder even at pH 2 can be attributed to the same phenomena by which chrome formate complexes can exist at pH values where there is very little ionization of the formic acids. Thus, two factors are again evident: the complex formation between the chromium and the ionized carboxyl group, and the ionization of the weak acid carboxyl group. As with chromium formate complexes, the first effect is dominant. The slight decrease of the sulfate fixed by the hide powder at higher pH values, as in-

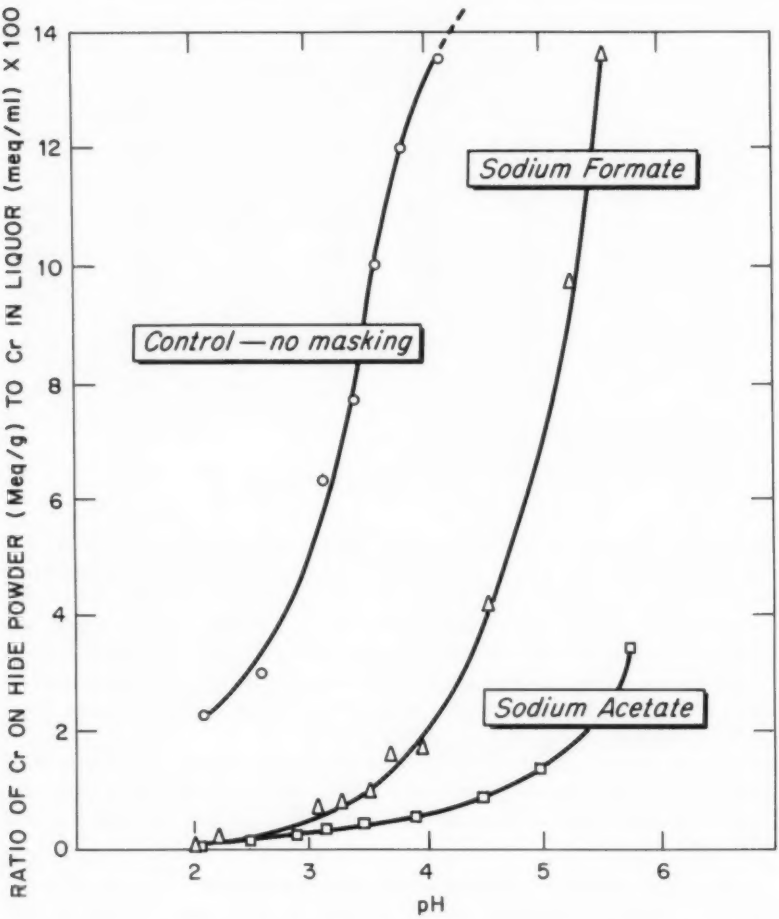

FIGURE 7.—The ratio of Cr on the hide powder (Meq /g) to Cr in solution (Meq /ml) X 100.

dicated here, may be due to several effects: the increase in basicity of the complex with increased pH, the removal of protein-bound sulfate at higher pH values, or the displacement of the sulfate from the complex by protein-acid groups. The curve showing the chromium ratio (the ratio of millequivalents of chromium fixed per gram to the millequivalents of chromium per ml. in the solution) rises very rapidly, particularly around pH 3.5 in keeping with practical tanning observations.

Sodium formate series.—In this series the effects of the formate in the system are evident to a great degree. There is a marked decrease in the fixation of the chromium at the lower pH values. There is also a decrease in the sulfate acidity of the chrome complex in the hide at the higher pH values. Here we can observe some of the same effects which were observed in formate-masked liquors in our previous study by ion exchange techniques.

Formate, in addition to sulfate and hydroxyl ions, can also compete with the carboxyl group of the hide protein for position in the chromium complex. The formate has been able to displace the protein particularly well at the low pH values. As the pH is brought above 4 there is a rapid rise in the ratio of the chromium fixed by the hide substance to the chromium remaining in solution. This indicates that at the higher pH values the hide protein gains an advantage in complexing power over that of the formate ion. This is also indicative of the need for tanning to higher pH values in formate tannage compared with unmasked liquors. Or, to put it another way, the hide protein-chromium complex is sufficiently stable at the higher pH values to prevent the detanning action of the formate ion.

Sodium acetate series.—In this series the same effects observed in the sodium formate series are present, but accentuated. The fixation of the chromium by the hide protein is decreased over the entire series, particularly at the lower pH values. With an increase in pH values there is more drastic displacement of the sulfate. The ratio between the chromium fixed by the hide substance to the chromium remaining in solution is considerably lower over the entire pH range than that obtained in either of the previous series. In confirmation of practical tanning observations, the use of sodium acetate results in a more stable complex than the protein-chromium complex over the entire practical pH range, and therefore little if any practical use has been made of acetates as masking agents. Although the hide protein may gain a relative advantage over the acetate at the higher pH value, there is an approach to the precipitation point at which no practical tanning can occur.

SUMMARY

The problem of the effect of masking salts in chrome tanning has been approached from the study of complex equilibria and solutions by means of ion exchange techniques and the study of detanning effects at various pH values. The following conclusions are drawn:

1. There is a competition between the protein carboxyl group, the sulfate, and the masking agent for coordinate positions in the chromium complex.

2. Coordination of weak organic anions, including hide carboxyl groups, may take place to a relatively large extent even in pH ranges where little ionization occurs. Increasing pH increases the coordination of weak acid anion masking agents.

3. The coordination of hide protein carboxyl groups is effected by pH changes to a greater extent than the coordination of the weak acid anions or formate and acetate. Substances forming complexes of great stability can effectively decrease tanning affinity regardless of the pH values used.

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Received April 11, 1957.

AMI FOUNDATION ADVOCATES FURTHER EXPLORATION OF AGENTS OTHER THAN SALT FOR PRESERVATION OF HIDES

Important hide research by American Meat Institute Foundation raises the question as to the efficiency of salt as a curing agent. As a result, AMI Foundation advocates that research on agents for preserving hides other than salt, is desirable since such research could prove economical and more effective.

The overall objective of this research is to develop protein constituents that might uncover new uses for hides.

This latest research has revealed that salt is not the ideal preserving or dehydrating agent. It is implied that there may be simpler and more effective ways of preserving hides other than with salt and AMI Foundation suggests that some recent bacteriocidal agents be investigated (either with conventionally produced hides or pre-trimmed and defleshed hides that have been thoroughly washed.)

The three primary functions of salt on brine curing are:

1. To remove non-leather-making proteins
2. To preserve the hide
3. To remove water

Research has revealed that a brine-cured sample showed that only 22.1% of the globular proteins had been removed and that a salt cured sample disclosed that only 15.6% had been removed. Therefore, the effect of salt curing in removing non-leather making proteins is limited. This discovery, in view of assumptions based on traditional utilization of the salt hide curing process, was not expected.

— *National Hide Association Bulletin*, April 9, 1957.

A SHEEPSKIN DEFECT: "SUMMER BLEEDING" DISEASE

J. J. Tancous, W. T. Roddy, and F. O'Flaherty

Department of Basic Science in Tanning Research
Tanners' Council Research Laboratory
University of Cincinnati

Recently there was a very unusual condition in a pickled sheepskin submitted to the laboratory for identification. The lesions consisted of some small irregular scars and a few vesicle-like swellings in the neck and shoulder areas of the skin (Figure 1). In this illustration the arrow marked "1" points to an area which represents a vesicle-like swelling, which is known as a bloody nodule, and the arrows marked "2" point to areas which show the scars that form when the lesions heal. This condition is encountered in foreign countries in both cattle hides and sheepskins; natively, it is referred to as "summer bleeding". It has been described by Král and Novak (1).

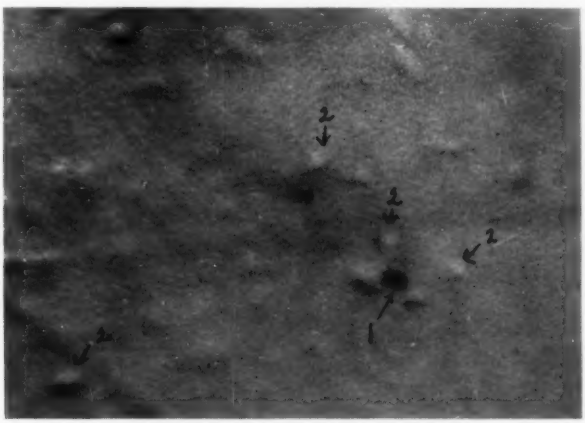

FIGURE 1.—Grain surface of a pickled sheepskin showing a bloody nodule (1) and scars (2) caused by "summer bleeding" disease. The nodule and scars are twice their natural size.

The lesions in the skin generally occur during the spring and summer; the wounds heal and the condition disappears in the winter. The parasite, a type of nematode classified as *Elaeophora Schneideri*, migrates from the muscles of the animal through the subcutaneous tissues and enters the skin

for the purpose of laying eggs. When this happens, there is subcutaneous bleeding, and a bloody nodule forms (Figure 2). This illustration is a cross-sectional view of the nodule; the dark area in the center of the section shows the presence of eggs and blood. Rupturing of the nodule causes the blood to come to the surface of the skin, and because this occurs in the summer the

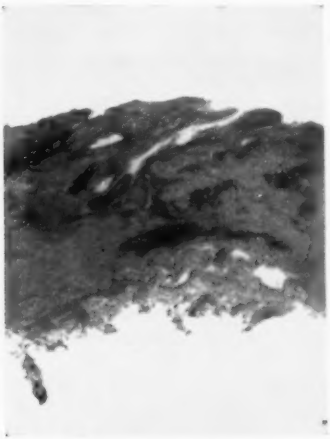

FIGURE 2.—Cross section through a bloody nodule which contains the eggs of the nematode responsible for the disease.

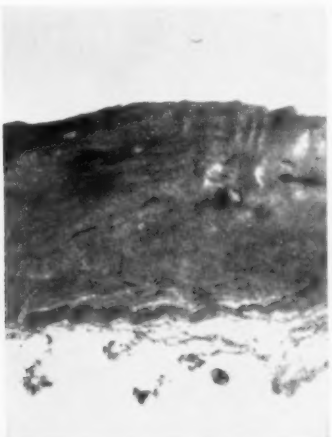

FIGURE 3.—Cross section through the scar tissue which forms after the lesion heals.

name "summer bleeding" was ascribed to the condition. The mature worms are thought to retreat into the deep parts of the skin; the eggs are discharged from the wounds, and flies swarming around the wounds act as intermediate hosts for spreading the disease. The complete life cycle of the parasite, however, is not precisely known. The disease usually recurs annually for 3 to 4 years, and then possibly an immunity develops.

When a wound heals, scar tissue forms (Figure 3). This is a cross-sectional view showing that the scarified area is deep in the skin tissue.

The worms, or nematodes, cause definite damage in leather. The bloody nodules are located in the corium of the skin, extending through to the epidermis, and the scar tissues are also deep-seated. The defect in the sheepskin studied consisted of a few small nodules about 2 mm. in size and many scars from healed lesions. The damage, whether in nodular form or as a scar, is evident in full-grain leather and cannot be eliminated even in suede leather due to this deep involvement of the tissues.

REFERENCE

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Received May 29, 1957.

For several centuries the art of decorating leather remained the specialty of Spain. The word "cordwainer," derived from Cordova, is a witness of this monopoly by the Peninsula of everything connected with leather-work, apart from the modelled and stamped leathers, introduced into Venice from the East.

—*The Decoration of Leather.* Maude Nathan. London: Archibald Constable & Co., Ltd., 1905.

Although it is certain that the process of vegetable tanning is exceedingly ancient, it is almost as certain that this was not the most primitive method, and that the curing of skins by smoke, by treatment with oils and fats, and by merely sun-drying, are methods even more ancient . . . . The manufacture of "tawed" or alumed leather was introduced at a much later date than the vegetable tannages, and was for a considerable period confined to a few localities in which the tawing materials were readily obtainable.

—*The Manufacture of Leather.* Hugh Garner Bennett. New York: D. Van Nostrand Company, 1910.

SOME ECONOMIC ASPECTS OF GRUB CONTROL*

FRED O'FLAHERTY

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Cincinnati, Ohio

Grub infestation in cattle has, in the past, been estimated as having caused a 100-million-dollar economic loss. Since records indicate that this parasitic disease is increasing, more recent estimates double the dollar loss and place it at 200 million dollars. This loss is primarily borne by the meatpacking and tanning industries.

A brief résumé of the life cycle of this parasite may help one to better appreciate the loss and to understand the complexity of eradication.

The grub is the larval stage of the heel fly, *Hypoderma lineatum* or *Hypoderma bovis*. Grubs are found in the cattle of every state in the United States as well as in Canada and Mexico.

The fly, which is about the size of the common housefly, lays eggs on the hair of cattle. The fly season varies with the climate, being earlier in the south and later in the north.

The eggs hatch, producing almost microscopic larvae which then penetrate the skin by way of the hair follicles; they pass to the flesh and there travel about in the animal for some months, during which metamorphosis occurs several times. The final stage arrives in the region of the back under the hide where they live for a number of months before making their exit and dropping to the ground. It is during these latter months that much of the damage is done to the meat and the hide.

When the mature larvae fall to the earth, they pupate and the flies emerge. The new life cycle is begun once more.

Each fly lays as many as 800 eggs before it dies. The time from laying eggs to the exit of the grub is 11 months—the entire life cycle being on an annual schedule.

There have been many materials reported which can be effective in killing the grub, mainly in the latter stages in the animal hide.

Derris powder, with its rotenone active principle, when applied to the larva in the hide, has proven very effective in killing the grub, but the damage has already been done to the meat and the hide.

Phenothiazine has been used in Europe and in the United States both alone and in combination with other chemicals. The results reported have been mixed, with no positive proof of its efficiency.

*Presented at the Fifty-third Annual Meeting of the American Leather Chemists Association, Lake Placid, New York, June 2–5, 1957. The discussion will be published in October.

If phenothiazine were to be made a uniformly effective larvacide, it would be very economical to use. It is fed with salt regularly. It is well established as an effective vermifuge destroying all varieties of roundworms in the intestinal tract; thus it would serve a double purpose. It is hoped that the proper form of phenothiazine can be found and a successful technique established.

More recently (1956) several organic phosphate compounds have been evaluated, and their efficiency has been demonstrated.

One such compound is Dow ET-57-(*o*,*o*-dimethyl-*o*-trichlorophenyl phosphorothioate). When administered orally in a dosage of 1.6 oz. per 1,000 lb. of animal weight, it has been highly effective in destroying grub larvae in the earlier stages and before they do any material damage to either the meat or hide.

Another compound of similar structure, Bayer's 21/199, which can be used as a spray, has also proven very effective. It is not known how this material gets to the larvae, but there is evidence that it can be absorbed by the skin.

The important fact about the organic phosphorus compounds is their ability to destroy the larvae in their early stages. This means that the life cycle is broken and the larvae destroyed before they do any material damage to the meat or the hide.

This then brings us to the economic aspect of the treatment. It is estimated that grub infestation costs the tanning industry alone more than 100 million dollars; the meat industry suffers an equal loss.

During the past ten years that the Hide Bureau of the Tanners' Council has kept records on the number of grubby hides received, there has been a gradual increase. It is more likely that the total economic losses suffered in consequence to grub infestation may be nearly a half-billion dollars.

This gigantic loss begins on the farm or range. During the fly season the cattle become wild with fright. The Department of Agriculture has listed the following effects:

(*a*) Reduction in milk yield and poor gains due to worry and interference with grazing. The reduction in milk has been estimated at 10 to 25 per cent.

(*b*) Loss in time due to difficulty in handling range cattle; it becomes difficult and sometimes impossible to move such cattle during the daytime.

(*c*) Physical injury to animals due to their frantic action. Animals have become mired in bogs and run off cliffs during such periods.

(*d*) After the larvae have entered the cattle, further losses begin.

Grub-infested cattle are unthrifty. Factual data are wanting on this aspect, but in an experimental lot there was a difference of 34 lb. gain in grub-free cattle versus an infested group. This loss occurred in one feeding season.

In dairy herds where daily records are maintained, the reduction in milk yield is most definite. A typical example was a good milker who gave an increase of 10 lb. of milk per day a few days after some 80 grubs had been removed.

At the packing house the damage to meat with its reduction in value of a trimmed side represents as much as $8.00 per head loss. It has been reported by Livestock Conservation that the meat loss averages $1.25 per head. Part of this cost is due to the most expensive cuts of meat being involved.

Hides, which are our main concern, undergo a most serious damage, and while the tanner suffers it most directly, it is reflected to every person who wears or uses leather.

The problem then resolves itself in, Who is to pay for such treatment and can it be expected to be repaid? It is the animal-husbandry man who must treat the cattle and do so about one month after the fly season is over for his respective area. It may be necessary to give two treatments if the full benefit is to be obtained. Then unless all persons in an area treat their animals, the benefit will be minimized. If cattle within a few miles are not treated and are grub-infested, there is every possibility that the grub-treated cattle may become infested too when the grubs of the untreated group become flies; therefore the treatment should be repeated each season.

Since we have never had any compulsory legislation on animal treatment, there is no guarantee that all cattle owners will treat their animals, especially if it is not factually established that the cost of treatment will pay the livestock owner a profit for his work.

It now remains for the economics of grub treatment in cattle to be established. The U. S. Department of Agriculture is the best organization to do this, and it is hoped that all industries concerned will urge that it make a factual evaluation of treating cattle for grub. With such information it would then be possible through education to eliminate the very serious economic loss now on the increase.

Received June 4, 1957.

LIFE LINES

Brief Biographies of Our Contributors

DR. AKIRA KAWAMURA was graduated from Kyoto Imperial University, Department of Agricultural Chemistry, Kyoto, Japan, in 1943. He was appointed Associate Professor of Agricultural Chemistry of Tokyo Noko Daigaku (Tokyo University of Agriculture and Technology), Fuchu, Tokyo, in 1950 and has studied on various chemical problems there, especially on analyses of chromium complexes. He was awarded a Ph. D. degree by Kyoto University—his thesis was "Studies on Chrome Tanning"—and was promoted this year to Professor of Agricultural Chemistry of Tokyo Noko Daigaku. He became an active member of ALCA in 1956 and now is a director of the Japanese Association of Leather Technology.

DR. FRED O'FLAHERTY—See the October, 1956, *Journal.*

WILLIAM T. RODDY—See the March *Journal* for the biography of this 1957 Alsop Award Winner.

MRS. JEAN JACOBS TANCOUS—See the July, 1956, *Journal.*

DR. THOMAS C. THORSTENSEN received his B.S. degree from the University of Minnesota and then served as chemist for the S. B. Foot Tanning Co. in Red Wing, Minnesota. After duty as shipboard engineering officer in the U. S. Navy during World War II he received his M.S. and Ph.D. from Lehigh University where he also acted as postdoctorate research associate under the late E. R. Theis. He then worked with the J. S. Young Co. of Baltimore, Maryland, as a research chemist on the development of synthetic tanning agents. At present he is director of the Tanners' Council Beamhouse Research Project at the Research Foundation of the Lowell Technological Institute. He has been an active member of ALCA since 1946 and is now chairman of the Raw Stock Evaluation Committee and Associate Editor of this *Journal.*

KEIZO WADA was graduated from Tokyo Noko Daigaku (Tokyo University of Agriculture and Technology), Department of Agricultural Chemistry, Fuchu, Tokyo, in 1949 and was appointed as an Instructor of Agricultural Chemistry there in 1953. Since 1949 he has studied with Dr. A. Kawamura mainly on the relations between chromium complexes and ion exchange resins. He is a Lecturer of Keisen Women's College, Kokubunzi, Tokyo, and a member of the Japanese Association of Leather Technology.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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SECRETARY'S NOTICE

A number of members have inquired whether it is possible to purchase glasses like those distributed at the banquet. These glasses can be purchased in sets of 8 for $7.95, if enough orders are placed. Any member who wishes to purchase one or more sets of 8 glasses at $7.95 per set please advise the ALCA secretary prior to October 1.

Courtesy the Leather Manufacturer

ABSTRACTERS MEET AT LAKE PLACID

Left to right: R. H. Twining, H. R. Wilson, I. D. Clarke, R. M. Lollar, H. Krakowski, J. M. Cassel, J. F. Wagoner, J. H. Highberger, T. D. Braunschweig, H. B. Merrill.

REPORT OF THE COORDINATOR OF TECHNICAL COMMITTEES*

COMMITTEE ORGANIZATION AND MEMBERSHIP

Vegetable Leathers: Arthur N. Kay, *Chairman*, R. G. Ashcraft, I. D. Clarke, S. Dahl, G. V. Downing, H. R. Miller, Jr., G. W. Schultz, J. F. Wagoner.

Tannin Analysis: Edward R. Rayfield, *Chairman*, R. B. Barnwell, M. Baum, T. Blair, I. D. Clarke (nonvoting), J. H. Davis, G. V. Downing, Ed-

*Submitted to the ALCA Council May 16, 1957

ward Facer, J. Jany, F. P. Luvisi, F. F. Marshall, R. L. Moore, Harold Nordstrom, L. Sheard, G. W. Stanberry, C. G. Telander (nonvoting), J. F. Wagoner, J. W. Wolfe (nonvoting). **Subcommittee on Determination of Lignosulfonates:** S. Dahl, *Chairman*; **Subcommittee on Nontannins in Lignosulfonates:** F. F. Marshall, *Chairman*; **Subcommittee on Waring Blender:** J. F. Wagoner, *Chairman.*

Hide Powder: I. D. Clarke, *Chairman*, Guido E. Daub, G. V. Downing, A. N. Kay, F. F. Marshall (nonvoting), G. W. Schultz.

Industrial Wastes: J. F. Wagoner, *Chairman*, G. A. Butz, W. C. Curtin, B. A. Grota, Jr., J. W. Harnly, M. M. Luckens, E. E. Presley, E. H. Stein, J. E. Tarman.

Mineral-tanned Leathers: N. C. Benrud, *Chairman*, R. S. Adams, Fred O'Flaherty, Tom S. Perrin, Ludwig Seligsberger, Robert Stubbings, Titus Weaver, Jesse Wendkos. **Subcommittee on Determination of Zirconium in Leather:** J. Wendkos, *Chairman*, L. Seligsberger, R. Stubbings.

Physical and Mechanical Properties: E. D. Compton, *Chairman*, J. R. Kanagy, W. T. Roddy, J. S. Rogers, and the chairmen of the following subcommittee and sections of the ALCA-ASTM Joint Committee on Physical Testing: R. G. Ashcraft (Subcom. 3, Sec. 4, Effect of Water), M. Baldwin (Subcom. 4, Research), G. A. Butz (Subcom. 3, General Physical Testing), A. N. Compton (Subcom. 3, Sec. 7, Mechanical Leathers), A. N. Kay (Subcom. 3, Sec. 10, Miscellaneous Physical Properties), R. M. Lollar (Subcom. 1, Nomenclature, Definitions and Applicability), C. W. Mann (Subcom. 2, Sampling and Conditioning for Physical Tests), J. Naghski (Subcom. 3, Sec. 2, Physical Dimensions), R. Stubbings (Subcom. 3, Sec. 5, Surface Characteristics), R. Young (Subcom. 3, Sec. 3, Tensile Properties).

Preparatory and Posttanning Processes: W. T. Roddy, *Chairman.* **Subcommittee on Fats and Oils:** Merrill Leach, *Chairman*, C. A. Blair, Ben A. Grota, Jr., V. Mattei, C. M. Morrison, Clinton E. Retzsch, T. Weaver.

Standards and Specifications: Carl G. Telander, *Chairman*, R. G. Ashcraft, M. H. Battles, Sverre Dahl, Ben A. Grota, Jr., Arthur N. Kay, Kenneth H. Knight, Robert M. Lollar, Charles W. Mann, E. E. Presley, R. L. Young.

Leather Finishes: Bernard Roll, *Chairman*, A. G. Fleisch, C. Paul McKee, Robert W. Osborne, Allen Phillips, Elwood Presley, Robert Shaw, Titus Weaver, Robert Welch, C. David Wilson.

Evaluation of Raw Stock: T. C. Thorstensen, *Chairman*, M. H. Battles, George Butz, F. L. DeBeukelaer, John Highberger, Jerome Jansing, R. I. Miller, E. J. Strandine, Robert Stubbings, C. David Wilson.

Mechanical Leathers Committee: H. V. Krakowski, *Chairman*, Arnold P. Barth, William Conn, James M. Thornton, Jack H. Van Sciver.

Representatives on International Commissions: *Hide Powder*, Ira D. Clarke; *Leather Analysis, Chemical*, Carl G. Telander; *Tannin Analysis*, A. N. Kay; *Physical Tests*, E. D. Compton; *Dyestuffs and Dyed Leather*, Bernard Roll.

At the meeting in January, Council voted to publish sheets for insertion in the methods book which will give the present status of our methods and all the changes which have been made in them since they were published.

The manuscript for such sheets has been prepared and checked by the various committee chairmen and is attached to this report.

There are two ways in which these sheets can be printed:

1. Separate sheets on white paper in which the up-to-date methods are tabulated as to status, and other sheets on which the required changes for each method are printed. These sheets could be placed in the methods booklet as a sort of separate section.

2. The status of each method and the required changes can be printed on colored gummed paper which is perforated so that each change can be torn from the sheet and pasted in the proper place in the methods book.

Council should decide which method of printing should be used.

Because so many changes were required in the methods of the B series, Council ordered that these methods should be reprinted, but that each reprinted method should carry the same number it now carries in the methods book. This is contrary to the recommendation of the Vegetable Leathers Committee which suggested that the first four B methods be renumbered. The reason for Council's action on this matter was that the methods of B series are referred to in a great many of the B series and other methods, and it was felt that renumbering would make a large number of changes which would not be necessary if the present numbers were retained. This is not true. Once the B methods are corrected, there remains only one other change, i.e., in Method D5 – 4.1, to be made. The objection to renumbering is therefore not valid, and it is suggested that Council's action be rescinded and the numbering system recommended by the committee be adopted.

The Method J40, Sampling of Tannery Chemicals, was approved by Council and ordered published as a Provisional Method. This has been held up so it could be sent to the printer with the methods changes.

At the meeting in January, the question was raised as to whether or not the Association should pay for some clerical assistance in doing the statistical work required in evaluating our methods and establishing sampling procedures. It was suggested that the writer prepare a more detailed statement of what he had in mind. Since that meeting two members of the Association have submitted suggested plans for improving our methods. These are in addition to the simple suggestion which was received from Dr. O'Flaherty last fall. Both plans are essentially the same. They consist in general of having the Association appropriate a sum of money to

1. Carry out a survey of leather producers and users to determine
   a) what failures in leather products commonly occur;
   b) what tests are used to determine these failures; and
   c) whether existing test methods are considered satisfactory for spotting such failures in advance, etc.

2. Conduct a general survey of consumers and producers to determine how much they use and have faith in our present test methods.

3. Conduct a general survey of procedures for sampling and evaluation of data which are used by consumers and producers to determine the properties of leather.

The writer cannot agree that such a survey should be financed by the Association. It seems that such things should be done either formally or informally by our present committees. If such a survey were made, the chief source of information would be our committee membership.

The plans which were presented indicate to the writer that if the Association starts the practice of giving substantial financial assistance to committees for even the most definite and simple purposes, there will be requests for aid for a growing number of things, all good and worthwhile, which could put a substantial burden on the Association.

The writer requests that the suggestion of giving extra financial aid to a sampling and evaluation committee be given no further consideration and that the whole matter be dropped.

M. MAESER
President-Elect

MINUTES OF THE VEGETABLE LEATHERS COMMITTEE MEETING

Lake Placid, N. Y.
June 2, 1957

The committee met at 3:10 P.M. Mr. Kay reported that the final revision of the B Methods was in Mr. Maeser's hands and would, he hoped, meet with Council's approval. All methods except B3 (Moisture) and B4 (Solvent Extract) had been recommended for adoption as official. With work still under way on B3 and B4, these two were recommended for retention as provisional.

Mr. Maeser had been asked for a clarification of par. 2.2 of Methods B8 (Water Solubles) and B20 (pH). It was agreed that the first part of the paragraph be changed to read: "If the leather contains more than 8% of material extractable by petroleum ether . . . . ."

The committee then discussed the problems facing Mr. Blair's Subcommittee on Moisture and Solvent Extract. In the case of moisture it is felt that the problem is largely one of definition, as indicated by Dr. Lollar's preliminary data, because of the equilibrium existing between free water, bound water, and water of constitution; hence, any end point will, of necessity, be arbitrary. Messrs. Lollar, Blair, and Kay are to look into the possibility of defining an acceptable end point and, if possible, a primary method of reaching it.

On solvent extract preliminary results by Dr. Lollar indicated that results depended on the boiling point of the solvent, rate of extraction, and time of drying. They also indicated, confirmed by preliminary results by Mr. M. H. Battles, that chloroform extracts a greater or lesser amount of nonfatty material depending on the amount and type of load present in the leather. It was therefore agreed that Mr. Blair's subcommittee should, as a first step, extract several types of leather with (*a*) chloroform, (*b*) carbon tetrachloride, (*c*) petroleum ether, and (*d*) hexane, on a statistical plan, to try to determine what differences exist.

ARTHUR N. KAY, *Chairman*

MINUTES OF THE PHYSICAL AND MECHANICAL PROPERTIES COMMITTEE MEETING

Lake Placid, N. Y.
June 2, 1957

Present were H. M. Baldwin, J. M. Cassel, E. M. Filachione, A. W. Hopton, M. Maeser, J. Naghski, E. G. Railo, W. T. Roddy, and E. D. Compton, *Chairman.*

The chairman reviewed the close vote of the committee on Methods E17, E31, E32, E42, E43, and E46. The committee agreed that these should be left provisional and referred to the appropriate subcommittee chairman of the Joint ALCA-ASTM Committee. Mr. Maeser reported that he had talked with Henri Krakowski, chairman of the Mechanical Leathers Committee, and pointed out that this committee should really fall in the Physical and Mechanical Properties Committee as it is now set up to coordinate work with the Joint ALCA-ASTM Committee. Mr. Krakowski had agreed. Mr. Maeser suggested that the chairman write A. N. Compton, chairman of Subcommittee III, Section VII (Mechanical Leathers), of the Joint Committee and invite him to become a member of ALCA and a member of the Physical and Mechanical Properties Committee. If he will not join ALCA then Jim Thorton should be invited to represent A. N. Compton's committee on the Physical and Mechanical Properties Committee.

Dr. Baldwin reminded the Committee that his subcommittee of the ALCA-ASTM Joint Committee is concerned with forming a list of methods now being investigated throughout the industry. He would appreciate all possible help in accumulating such a list.

J. Naghski, chairman of Subcommittee III, Section II (Physical Dimensions), reported that his subcommittee has considered four ALCA methods: E2, E3, E4, and E5. E2 and E5 were reviewed and rewritten in the ASTM format. E3 and E4 are being studied further.

E. D. COMPTON, *Chairman*

MINUTES OF THE STANDARDS AND SPECIFICATIONS COMMITTEE MEETING

Lake Placid, N. Y.
June 2, 1957

The meeting was called to order at 2 P.M. Members present were R. G. Ashcraft, M. H. Battles, S. Dahl, B. A. Grota, A. N. Kay, R. M. Lollar, C. W. Mann, E. E. Presley, R. L. Young, Jr., and Carl G. Telander, *Chairman.* Guests were C. W. Beebe, C. Blair, I. D. Clarke, G. V. Downing, J. M. Hinkle, F. P. Luvisi, M. Maeser, F. F. Marshall, N. F. Marshall, G. L. Somer, and J. F. Wagoner.

The chairman reviewed the question of various government agency specifications on leather and the suggestion made in 1955, directed to the General Service Administration, that they be unified. Mr. Mann reported that the effort towards standardization continues.

Mr. Mann presented his draft of a report on area vz. weight basis sampling of sole leather. The report showed again that there is no significant difference in results when sole leather is sampled and composited on either area or weight basis. The committee unanimously agreed that for the sake of simplicity and to minimize sources of error sole leather should be sampled on an equal area basis by the use of a die. Dr. Lollar moved, seconded by Mr. Kay, that the preliminary analytical data presented by Kay and Telander should be included as an addendum to the report, which should then be completed and resubmitted to the full membership of the committee prior to request for publication. The motion carried.

Mr. Blair reported that the subcommittee for re-examination of analytical methods for moisture and grease determination had not been organized. The Standards and Specifications Committee has a vital interest in these questions since they reflect directly on the specifications limits. Until these methods are agreed upon between the ALCA and the Bureau of Standards, this committee can not act. The question is the responsibility of the Vegetable Leathers Committee, which will direct the work.

A method for the alkali solubility of leather-cellulose mixtures had previously been submitted to the committee for recommendations and approval The chairman has received no objections to the method as proposed. Mr. Kay suggested that the specimen for analysis should be extracted with water after the grease extraction and prior to hydrolysis so as to remove sugars, inorganic salts, etc. The hydrolysis should then be conducted with slightly stronger alkali on the wet specimen. The method was approved in principle, and the chairman was authorized to make the above suggestion to the Bureau of Standards.

Mr. Young pointed out the desirability of expressing physical testing data on a common basis and cited as an example the specification limits for stitch tear test on gusset leather, where it is expressed in lb. per inch thickness, whereas for other leathers it is expressed in lb. pull per specimen of given dimensions. The chairman was authorized to contact the Bureau of Standards' Leather Section and suggest that the question should be considered.

Mr. Mann discussed the test methods for crocking of leather and the need for review of the test methods as well as expression of the results. The chairman reported that the test methods are under consideration by the Physical Testing Committee.

The committee membership was reviewed and approved as of this meeting. The chairman was re-elected for the ensuing year.

CARL G. TELANDER, *Chairman*

ABSTRACTS

Structure of Gelatin. VII. Evidence of Modification of Structure during Hydrolysis in Isoelectric Solution. J. Pouradier and A. M. Venet. *J. Chim. Phys.*, **53,** 778–81 (1956); *Chem. Abstr.*, **51,** 4797*i*.

Denaturation of Gelatin by Formaldehyde. J. Pouradier and H. Chateau. *J. Chim. Phys.*, **53,** 726–31 (1956); *Chem. Abstr.*, **51,** 4798*a*.

Thermal Treatment of Fleshing (for Gelatin Manufacture). A. Bycichin, J. Lacnak, and B. Nemec. *Kozarstvi*, **6,** 50–52 (1956).—The usual time of liming of fleshings, said to be 3 to 6 months, can be shortened to 7 days by pretreatment for 5 min. in boiling water. In experiments with steerhide and pigskin fleshings the volume of the fleshings diminished by 22 to 27% after 2 min. immersion in water at 66° to 76°C. Immersion in boiling water for 0.5 to 10 min. caused a weight loss of 15–17%, due to shrinkage, as only 2% of gelatin was dissolved. Extraction of gelatin at 70°C. from the thermally pretreated, limed fleshings proceeds 8 times faster than normal. The quality of gelatin produced is normal, except that the fat content is higher. Fleshings must be cut to uniform size before the thermal treatment. L.M.

Microbiology in Tanning. P. Safarik. *Kozarstvi*, **6,** 105–6 (1956).—The preservative action of salt in curing is due to plasmolysis of cells of microorganisms. Red heat is caused by purple sulfur bacteria and by some species of Torula. Destruction by tannase of tannin in tan liquors, which may amount to 6%, is brought about by many molds. Formation of acid in tan liquors is studied. White spots on hide in suspenders are caused by a slimy fermentation brought about by *Leuconostoc mesenterides, L. dextranicum, B. mesentericus fuscus,* or *Alcaligenes viscosus.* Mold enzyme bates are mentioned. L.M.

pH Factor in Washing of Hair and Bristles. J. Jezek. *Kozarstvi*, **6,** 122–24 (1956).—The following procedure is recommended for use in textile factories: Wash 15 min. at 50°–60°C. in Na_2CO_3 solution at pH 9.5–10, with the addition of K soap or sulfated higher alcohols. Add a CCl_4 emulsion before the end of the wash. Drain, wash the bristles with water, and acidify to pH 4–5 with HCOOH. Bleach with H_2O_2 plus NH_4OH, with pH stabilized at 7.5–8.0 with Na_2SiO_3, followed by a reduction bleach with Rongalite ($NaHSO_2 \cdot CHOH \cdot 2H_2O$). L.M.

Pilot Plant Production of Prechromed Sole Leather. I. Binko and K. Müller. *Kozarstvi*, **6,** 25–27 (1956).—The pelts were pickled, lightly Cr-tanned, and then drum-tanned 6–8 days in 150% of 110° Bk. liquor containing 30–50% syntan. The spent liquor (Bk. 40°–45°) contained 2.5% tannin. Attempts to reduce tannin loss by lowering the initial concentration to 70°–90° Bk. were unsuccessful; the liquor was exhausted to 0.35% tannin, but the leather

was drawn and not struck through. Two suspender liquors were introduced before drum tannage, made up with liquor (Bk. 40°–50°) drained from the drum (drum liquor initially was Bk. 120°). The suspender liquors were exhausted to Bk. 15°–20°. The pH of drum liquors was about 3.0. The leather contained 0.4–0.8% Cr_2O_3. Hydrothermal stability of leather at 50°C. was 81–92%. The method is inferior to normal pit tannage. L.M.

Production of Chrome-Vegetable-tanned Sole Leathers in Czechoslovakia. III. M. Tomisek, L. Kucka, and M. Minarek. *Kozarstvi*, **6,** 48 (1956).—A final pilot plant test was made. The Cr_2O_3 content was lowered to 0.75%. Tannage was done in 3 suspenders and 3 drums; Bk. 7°, 27°, 46°, 66°, and 98°; tannin/nontannin 0.635, 0.784, 1.614, and 2.483; pH 3.5–3.65. L.M.

One Hundred Best Water and Sewage Books (for Engineers, Chemists and Plant Operators). Harry A. Faber. *Water and Sewage Works*, **104,** 160–61 (1957).—This list, compiled from replies to a questionnaire, is broken down into 6 groups, with some duplicate listings, as follows: (1) general water and sewage, 19 titles; (2) engineering and hydraulics, 18; (3) water supply and treatment, 19; (4) sewerage and sewage treatment, 17; (5) industrial water and wastes, 11; and (6) laboratory analyses and control, 19. J.F.W.

Damage to Pelt Caused by Overheating during Drying. R. G. Mitton and C. D. Pomeroy. *J. Soc. Leather Trades' Chemists*, **41,** 109–14 (1957).—Freshly flayed sheepskin from which wool was removed was cut into small squares which were then placed in salt solutions of various concentrations. After prescribed times in the salt solutions specimens were washed in cold water and placed in a lime bath. The ease with which specimens tore before and after liming was recorded. Little or no loss in strength occurred on liming samples previously heated in the salt solutions to any temperature up to 2 to 3 degrees below shrinkage temperature. Of the salts compared only solutions of magnesium chloride showed any marked effect, the damage increasing with concentration. A second skin was experimentally damaged by overheating during drying. Drying was found to cause damage if the temperature was allowed to rise to 65°C. or more toward the end of drying. Damage is likely if the wet skin temperature exceeds 50°C. A test for crackiness is suggested to help in deciding before processing whether skins have been heat-damaged during drying. J.M.C.

The Composition of Epidermis. J. H. Bowes and R. G. Elliot. *J. Soc. Leather Trades' Chemists*, **41,** 87–93 (1957).—Epidermis was separated from flayed oxhide by treatment in water at 60°C. Any remaining hair in the epidermis was removed with tweezers, after which the material was degreased and dried in air. Determinations were made of ash, moisture, total nitrogen, amide nitrogen, and total sulfur. An amino acid analysis accounting for 89% of the total nitrogen was performed by column chromatography. Sulfur was accounted for entirely as cystine–cysteine (not separated) or methionine.

The composition of epidermis is shown to differ appreciably from that of typical keratins such as wool, hair, and horn in that the epidermis is very low in cystine and is relatively low in proline, threonine, valine, and arginine. Epidermis is higher in methionine, glycine, lysine, aspartic acid, and histidine. The swelling and solubility of epidermis in sodium hydroxide solutions (pH 12.3) are much greater than that of wool or hair. Water uptake and solubility of all three proteins are much increased in sodium sulfide solutions of the equivalent pH.
J.M.C.

The Influence of Small Quantities of Oil on the Tensile Properties of Vegetable-tanned Split Hides. C. D. Pomeroy. *J. Soc. Leather Trades' Chemists*, **41**, 106–8 (1957).—Degreased vegetable-tanned split sides were treated with acetone solutions of sulfated mineral oil so that 0 to 32% oil was added. As little as 1% oil was found to increase appreciably the tensile strength, breaking load, and percentage elongation at break. These tensile properties were all increased with increased deposition of oil up to 16%. Small oil additions are said to be sufficient to affect interfibrillary adhesion, and this supports the theory that the decrease in rate of abrasion of sole leather resulting from degreasing is due to the removal of lubricants between fibers. A subsidiary experiment employing mineral, cod, and oleic acid oils gave similar results.
J.M.C.

Chemical Study of Components Making Up the Lime Liquors and Their Relation to the Swelling of Skin. J. M. Santamaria. *Bol. Asoc. Quim. Espan. Ind. Cuero*, 1956, 277.—Factors affecting the swelling of pelt in lime liquors are studied. Swelling increases with increasing concentration of OH^- and Ca^{++}, with the ratio of monovalent to divalent cations, and with the difference in ion concentration between the interior of the skin and the external solution. These facts lead to complex interactions. Addition of NaCl increases the solubility of lime. Differences of opinion as to the effect of adding small amounts of NaCl to lime liquors may be due to the salting out effect on the suspended $Ca(OH)_2$, which may cause failure to attain saturation if agitation is not sufficient. Addition of $CaCl_2$ reduces swelling by depressing the solubility of lime, increasing the ratio of divalent to monovalent ions, and decreasing the difference in ion concentration between pelt and liquor. Addition of Na_2S increases swelling because the effects of increased OH^-, decrease in Ca^{++}, and increase in ratio of monovalent to divalent ions more than offset the decrease in ratio of external to internal ion concentration. Addition of NaHS has similar but less marked effects on swelling. The author has had excellent results with conventional lime liquors containing added salt to repress swelling.
H.V.K.

Studies on Tanning with Monolayers. H. Kayikama and H. Kamei. *Repts. Govt. Chem. Ind. Research Inst., Tokyo*, **52**, 17–20 (1957) (English summary).—Gelatin and ovalbumin monolayers on NaCl or $(NH_4)_2SO_4$ solutions were studied. The surface tension of the gelatin monolayer is the greater when distended, and that of the ovalbumin monolayer is the greater when the films are compressed. This is thought to indicate a more packed structure for ovalbumin films. Both monolayers were tanned by tannic acid but not by gallic acid or phloroglucinol.
H.B.M.

Comparison of Different Methods for the Determination of the Chromium Content in Leather. E. G. Masanella. *Bol. Asoc. Quim. Espan. Ind. Cuero*, 1956, 295.—Side leather samples were analyzed in triplicate or quadruplicate for Cr_2O_3 by 3 methods, with the following results: fusion (borax 1, Na_2CO_3 1, K_2CO_3 1) 4.01–4.07; $HClO_4$, 4.07–4.15; persulfate, 4.03–4.17. The perchlorate method is preferred. H.V.K.

Tanning Materials and Vegetable Tannage. M. B. Capreras. *Bol. Asoc. Quim. Espan. Ind. Cuero*, 1956, 271.—Short résumés of different European South American, and American techniques in tanning sole leather. H.V.K.

The Salting of Slaughtered Hides. *Cuoio, Pelli, Mat. concianti*, **33,** 23–26 (1957); see *Leder und Häutemarkt*, No. 3, 20 (1957).—The German Society for the Improvement of Hides has suggested the following specifications for the salting of slaughtered hides: Salt for light hides shall have grain sizes less than 0.5 mm., 20–30%; 0.5 to 1 mm., 30–50%; and from 1 to 2 mm., 20–30%. For heavy hides the grain size shall be: less than 1.04 mm., maximum 45%; 1.04 to 2.45 mm., minimum 47%; over 2.45 mm., maximum 7.5%. The content of NaCl is 98–99%; soluble Ca and Mg salts (calculated as sulfates), maximum 1% in the salt for light hides and 2% for heavy hides; insoluble matter, maximum 0.5%; Fe_2O_3, maximum 0.03%; and moisture, maximum 2%. The denaturants proposed are: 0.1% petroleum or 0.25% mineral oil; 2% soda ash; and, in the period from April 1 to October 31, 1% naphthalene. The salting shall be done immediately after slaughtering the animals when the hides are cold; light hides are salted with 50% of their weight of salt, heavy ones with 40%. The salt shall never be reused. G.A.B.

The Mechanism of Action of Oils on Hide Substance. R. Airoldi. *Chimica e industria* (Milan), **39,** 213–19 (1957).—Several hypotheses already proposed for explaining the mechanism of oil tannage are critically reviewed. Following the oldest experiments made in this field (Fahrion, 1915; Mothur, 1927), oil tannage was considered to be a reaction between the NH_2 groups of the protein and the peroxides formed in the oxidation of a fatty acid containing double bonds. Only acids with 2 double bonds may act as tanning materials; it is supposed that one of the 2 bonds is broken giving a peroxide ring which then combines with the protein, while the other double bond is broken giving a lactone derivative that is mechanically absorbed by the hide. The compounds catalyzing the oxidation (Pb, Cu, Mn, Co salts; Na_2O_2, $K_2Cr_2O_7$, and other oxidizing compounds) increase the speed of the tannage; on the contrary, the addition of an antioxidizing compound (e.g., quinone) to oils showing a tendency to produce resins during the chamois tannage is suggested (cf. the experiments of Chambard and Durande-Ayme). Many authors (e.g., Küntzel) believe that oil tannage is due to the presence of aldehydes, particularly acrolein, which is formed in the autooxidation of the oils from marine animals. It is possible that the reaction with the peroxides and that with aldehydes take place contemporaneously. The best oil for chamois tannage is cod-liver oil, but in general the oils with relatively high Acid No. and low I_2 No. show good tanning properties, and the oils having strong tanning activity do

not show the tendency to resinification (cf. Stather and Sluyter). According to recent studies (cf. Sagoschen and Czepelak) the aldehydes having tanning power give a less soft and more colored leather than that obtained by the action of fatty acids. The oil tannage may be considered as a chemical process, and specifically as the product of the reaction of collagen with some transformation products of nonsaturated glycerides contained in the oils of marine animals, but till now the chemical compounds acting in this reaction have not been exactly determined, and it is not sure that acrolein is indispensable to oil tannage. 50 references are appended. G.A.B.

Suggestions for the Manufacture of Chamois Leather. A. Simoncini. *Conceria*, **65,** No. 2662, 27–31 (1957).—To obtain good chamois leathers the grain side may be eliminated, because it may hinder the obtaining of a sufficiently soft leather; moreover the absorption of the fats takes place more easily when the grain is removed. Liming may be done in 2 stages, using first an old lime bath for 4–5 days, followed after splitting the hides by a fresh lime bath for 2 days. Complete deliming and bating follow; then the hides are allowed to dry partially in order that they may lose the greater part of the moisture. For the tannage it is necessary to use a fish oil with I_2 No. between 135 and 165, and Acidity No. between 15 and 20. When the I_2 No. is greater than 165, the tannage is too rapid, and the hides are stiff and fragile; when it is less than 135, the tannage is too slow. The best oil is cod-liver oil which gives yellow leathers, light and soft. For thicker hides the oil is given in several portions; for the light ones, in only one. The hides are laid out on a table, greased and folded, placed in the drum and turned 2 hr., opened to facilitate the oxidation and again turned 2 hr. During these operations there is a development of acrolein. The hides are then piled up to dry, and it is essential that the temperature shall never be higher than 40°C. The amount of oil used is 100–150% calculated on the pelt weight, but the maximum of combined fat in the hides is 10–15%. Degreasing of the tanned hides is made at first mechanically with the knife, and then with a tepid solution of Na_2CO_3 or K_2CO_3. Sometimes the hides become brown instead of yellow, and in this case they may be dipped rapidly into a 0.15% solution of $KMnO_4$, then washed in $NaHSO_3$ solution. G.A.B.

Formation of Colored Spots on Leather by Microorganisms. H. Martin. *Bull. Assoc. Franc. Chimistes Inds. Cuir*, **18,** 175 (1956).—For several years, varicolored spots have appeared periodically on basils for linings tanned around Graulhet and Mazamet. These accidents are caused by the action of a number of microorganisms growing on the raw or tanned skins or in the tan liquors. A number of these microorganisms have been isolated and identified. The same colored spots observed in the tanneries have been reproduced experimentally, using purified stock cultures. A description is given of the character of the discolorations and their differentiation from accidental discolorations by metal salts. Fermentation and the effects caused by bacteria, fungi, and molds are explained. Suggestions are made for antiseptic prevention of discolorations caused by microorganisms. T.D.B.

Presentation of a Modern Chrome Tanning Procedure. Shammon. *Rev. Tech. Inds. Cuir.*, **48,** 205 (1956).—The process refers to chrome side

leather made from hides weighing 45 to 55 lb. Soak by hanging in pits for a total of 48 hr. in two waters of 18°–22°C. It is better to prolong the soak by suspension instead of mechanical agitation. Deformations and distortions of the fiber in the initial stage are irreparable. The hides are green-fleshed out of soaking to facilitate unhairing. For unhairing, a drum running at 1 rpm is preferred. Great labor economy is obtained by loading from the top and unloading on a ramp. At 20°–24°C., unhairing is complete after 48 hr. The drum runs a few revolutions, hourly at the start but at longer intervals later. As a basic formula, 4% hydrated lime and 1% each of Na_2S and NaHS, based on drained fleshed weight, are recommended. The hides are taken from the drum without washing to avoid a sudden change of pH on the surface, causing drawn grain. After unhairing, according to the nature of the hides and the desired softness, the hides are suspended for 48 hr. in a fresh plain lime for better scudding, to reduce the pH gradually, and to facilitate the removal of sulfides. After lime splitting, a paddle is recommended for deliming, bating, and pickling, because it allows closer control. After the pack is put in the paddle, the temperature is adjusted to 33°–34°C. and a deliming agent (lactic acid or a buffered stronger acid) is added, followed after a few minutes by a bate concentrate (free of deliming agent). Separation of deliming and bating in this way permits easier control of the operations. While the pH in the float should be 8.2–8.3 at the end of the deliming and bating process, cuttings from the flank should still show a strongly red center streak against phenolphthalein. Only the surface layers should be delimed and bated.. The temperature is gradually reduced from 33°–34° to 18°–20° by washing. Salt is added to obtain a brine of 5°–6° Bé. After 30–45 min. 0.8–1.0% sulfuric acid (66° Bé.), previously diluted, is added and the paddle run for another 15 min., then stopped overnight. The next day, after running briefly, the pH of the pickle should be 2.8–3.5. Cuttings from the flanks tested with bromecresol green should indicate a blue center between two narrow yellow outer layers. The sides, after draining, are ready for the tannage. After such a preparation the grain will not react brutally with the Cr salt. If little salt is used in the pickle, the hide does not lose too much in plumpness, the fibers are not oriented too horizontally, and they are fixed in this condition by the first chrome feed. The center of the hide is most reactive and, with the chrome increasing in basicity as it penetrates, fixation is rapid. This results in a smooth grain and a full side. The salts left in the center of the skins act as masking agents without impeding the tannage. If wanted, an additional masking agent (Na or Ca formate or phthalate) may be given. Starting the tannage in a liquor of low density (2°–3° Bé.) will cause the hides to swell slightly. The first feed, at 33–38% basicity, is rapidly exhausted. The second feed is given at 45% basicity about 15 min. later; the last feed, at 50% basicity after another 30 min. The drum runs for a total of 9 hr. and rests overnight. After running briefly the next morning, the sides are removed. Generally, no basification should be needed, but if this should be necessary, it must be done promptly after the last feed, otherwise the alkali will find a liquor too low in Cr, will raise the basicity brutally, and cause a drawn grain.

T.D.B.

Study on Liming Conditions. Influence of Temperature. 3 (cont.) R. Lasserre. *Bull. Assoc. Franc. Chimistes Inds. Cuir.*, **18**, 243 (1956); see *JALCA*, **52**, 106 (1957).—In this part limes with a greatly increased sulfide concentration are compared with the previous tests in order to come close to

the rapid unhairing presently practiced on heavy hides. Two experiments have been added to the standard sequence set up at 8°, 20°, 30°, and 37°C.:

a) at 20°C. the hide is removed after 24 hours from the lime, and
b) at 20°C., after liming for 24 hours in the lime-sulfide solution, the hide is moved to a plain lime for another 24 hours.

In all instances Na_2S concentration is 5% and lime concentration 15 g/l.

At 37°C. unhairing starts in patches after 2 hours, similar to the action of plain Na_2S. At lower temperature the hairy patches become increasingly larger. After 3 hours the hide in the lime at 37° is completely unhaired but is left in the lime for the full 18 hours like the samples at lower temperatures. At this point all samples are unhaired but still show patches of scud which are then partly eliminated by graining with a slicker. The hides have a maximum plumpness at 8°, which decreases somewhat in the limes at higher temperature. The hair is severely attacked and dissolves in the lime but not as rapidly as in a bath of plain Na_2S of equal concentration. After deliming, no great differences can be observed between the various tests. If the hide is passed into a plain lime, a decrease in thickness as well as in the amount of water causing the swelling is noticed, yet there is an increase in weight. To explain this it is assumed that swelling of the fibers increases, retaining less water, while the water retained in the interfiber spaces is increased. Losses of hide substance at low temperatures are similar to those observed in plain sulfide baths, but at 30° hydrolysis of the hide is more pronounced, which might be explained by the higher alkalinity maintained by the presence of lime. Actually, in plain sulfide the pH drops to 11.8, while in a lime-sulfide bath the pH is maintained at 12.6. This difference of alkalinity appears mainly at 30°. At 37° losses in hide substance are practically the same in both instances, which indicates that temperature is of greater importance than alkalinity. Histological examination shows an increasing separation of the fibers with increase in temperature. The shaft hair is attacked and breaks off at the hide surface. With increased temperature this decomposition of the hair proceeds deeper into the hair follicle. T.D.B.

The Drying of Leather. *Das Leder*, **7**, 241–51 (1956).—A symposium on drying introduced by the following 4 papers: **Air Circulation and Hygroscopic Equilibrium.** H. P. Leistner. 241–45.—A discussion of general principles; automatic controls for regulating temperature and relative humidity; and air changes, distribution, and velocities. **Significance of Humidity in Drying Chrome Upper Leather.** H. Freudenberg. 245–47.—Graphs show the moisture content of leather at various relative humidities, and that the temperature of the leather surface is constant until capillary water has evaporated, after which it rises gradually. **Drying Leather that Contains Large Amounts of Soluble Matter.** R. G. Mitton. 247–48.—A discussion of the migration of solids to the leather surface during drying. [See *Some Aspects of the Drying and Heating of Textiles. III. The Migration of Solvents and Solutes during Drying.* Preston *et al. J. Soc. Dyers and Colorists*, **64**, 60 (1948)]. **The Change in Rate of Evaporation of Water during Leather Drying.** P. J. van Vlimmeren. 248–51.—The curve showing water content versus rate of drying consists of 3 portions: (1) a horizontal (constant) portion while capillary water is present, then falling portions during (2) evaporation of water within the leather rather than on its surface, and (3) loss of bound water. I.D.C.

The Configuration of Polypeptide Chains in Proteins. R. B. Corey and L. Pauling. *Rend. Ist. Lombardo Sci. Pt. I.*, **89,** 10–37 (1955); *Chem. Abstr.*, **51,** 7457*f*.

Black Tea Tannin. III. Fractional Determination of Black Tea Tannins. Y. Oshima, T. Nakabayashi, and S. Ishabashi. *Nippon Nogei-Kagaku Kaishi*, **28,** 614–18 (1954); *Chem. Abstr.*, **51,** 7482*g*.

Specific Determination of Proline in Biological Material. A. E. Pasieka and J. F. Morgan. *Proc. Soc. Exptl. Biol. Med.*, **93,** 54–57 (1956); *Chem. Abstr.*, **51,** 7483*i*.

Leather Bookbindings—How to Preserve Them. J. S. Rogers and C. W. Beebe. *U. S. Dept. Agr. Leaflet*, **No. 398,** 8 pp. (1956).

The Interaction of Gelatin with Lead Ion. T. Tachibana, K. Tamamushi, and R. Tamamushi. *J. Biochem. (Tokyo)*, **44,** 33–45 (1957); *Chem. Abstr.*, **51,** 7748*h*.

25 Years of Leather Finishing with Dispersions of Plastics. G. Otto. *Das Leder*, **7,** 252–58 (1956).—A history of the development of leather finishes. First pigment finishes based on shellac were used, then nitrocellulose lacquers, synthetic polymers, and finally, emulsion finishes, especially Corialgrund E (polyacrylic acid methyl ester) and Corialgrund N (sodium salt of polyacrylic acid). I.D.C.

Train Oil Oxidation Products Formed under the Conditions of Chamois Tanning. III. The Theory of Train Oil Tanning.—A. Küntzel and Th. Nungesser. *Das Leder*, **7,** 298–305 (1956). (See *JALCA*, **51,** 684 [1957].) The characteristics of chamois leather, and methods and theories of chamois tanning are reviewed. A theory must explain the insensitivity of chamois leather to alkali (a characteristic of aldehyde tannages) and the content of nonextractable fat that is either chemically bound or mechanically fixed on the fiber surfaces. I.D.C.

The Determination of Chromium and Iron Contained in the Leather Only as a Tanning Material. A Simoncini and M. Gelsomino. *Cuoio, Pelli, Mat. Concianti*, **33,** 7–12 (1957).—In researches on mineral-tanned leathers it is often necessarry to determine the amount of metallic oxides combined with the protein, but when these leathers are finished with finishes containing inorganic pigments, the determination may be difficult or even impossible. Several methods were suggested for this purpose. Digestion of leather in solutions of compounds hydrolyzing only the leather and dissolving only the metallic oxide

combined with the protein (glycolic, formic, and trichloroacetic acids) is complex and unpractical. Removal of the film with organic solvents gives only partial results, or it may happen that the solvent carries some particles of the pigment into the upper grain of leather. The mechanical removal of the film with the buffing machine gives imperfect results. It is now suggested to use an apparatus already proposed [*JALCA*, **51,** 622 (1956)] to buff the leather with a spray of finely powdered quartz (not with carborundum, which may contain Fe). By operating with care, it is possible to remove exactly the finish film from the surface of the leather without attacking the inner hide substance. Several analyses show that, in the case of chrome leathers finished with Cr pigments, the maximum error in the Cr determination when this method of removing the finish is used, is 0.03%, while with other methods the error reaches 0.30%; with chrome- and iron-tanned leathers finished with Cr and Fe pigments the maximum errors were 0.04% and 0.02%, and with the other methods 0.25% for Fe and 0.34% for Cr. G.A.B.

The Graphical Representation of the Tannery Processes. R. Stratta. *Conceria*, **65,** No. 2678, 16–20 (1957).—Only occasionally are diagrams showing the scheme of a given process used in the tanning industry, and till now no plant schemes were published because of the difficulty of representing in a simple way the numerous and often complex machines employed in tannery work and the relative operations. Several suggestions are given to extend the use of these plant schemes, indicating the various kinds of equipment forming the complete working plant (machinery, pipes, electrical equipment, etc.) with simple symbols easy to draw and to undertand which are now proposed for adoption by the Italian Chemical Unification Committee. Several examples are given. G.A.B.

Modern Points of View of the Problem of Production: Applied Research and Collaboration. A. Simoncini. *Conceria*, **65,** No. 2677, 35–8 (1957).—The problems issuing from the modernization and automatic control of the production processes are briefly reviewed. In the tanning industry the application of these principles does not seem easy if they are not preceded by a closer collaboration between the research staff and the technical executive one. Recently some Italian tanneries which have introduced for the first time these principles got an increase of production varying from 10 to 35%. G.A.B.

The Dyeing of Glove Leather. R. Vrbacky and (Mrs.) V. Vrbacka. *Kozarstvi*, **6,** 180–83, 194–97 (1956).—The effect of pH was studied. In dyeing glove leather, pH varies from 3 to 9. The work of Belavsky and Kratky (*C. A.*, **32,** 6497[8]) and Pektor and Radil (*C. A.*, **49,** 7280*e*) is referred to; the latter authors studied the effect of pH on dyes at pH 1 to 11. Changes in hue with pH were studied with a photocolorimeter, and results are tabulated. Mixtures of dyes, even those containing minor amounts of shading dyes, give most trouble due to changing pH, because of different penetration, especially with suede. Small-scale tests are difficult to translate into production. Chroma-

tography of dyestuffs is recommended [see Grassmann and Hübner, *JALCA*, **49,** 641 (1954)]. Ascending chromatograms were made on S & S. 2043B paper, 200 x 300 mm., using 1% aqueous solutions of acid and direct dyestuffs, spotted 30 mm. apart and 25 mm. from the lower edge. The lower 10 mm. of the paper is immersed in developing solution. Rf values vary greatly with pH value. For controlling pH, solutions of acetic acid, its salts, and ammonia were used. Two-way chromatography gives still better results. For circular paper chromatography Grassmann's method (*loc. cit.*) was changed by using a paper wick to draw the solution onto the paper. Paper electrophoresis was used for studying ionized compounds. Overheating causes concentration of the components in the center of the paper. An EMF of 100 volts per cm. is recommended. A plexiglass cuvette, with carbon electrodes located under the paper, was developed. For studying the affinity of dyestuffs to leather the method of Franz and Latinek (*C. A.*, **49,** 9352*e*) which gives the relation between Rf and dipole moment, and that of Schweitzer and Lollar [*JALCA*, **47,** 140 (1952)] are recommended. Chromatography of dyestuffs on leather was attempted using a disk of washed, neutralized, wet, Cr-tanned goat leather. The dye solution was applied at the center of the disk. Because the leather was already wet, Rf values, i.e., ratio of travel of dye to travel of solvent, could not be determined, so relative Rf values were measured, taking Rf of Orange GG as 1. L.M.

Microscopic Changes in Skins during Their Manufacture. R. Böhm. *Kozarstvi,* **6,** 82–83 (1956).—Brining has little effect on appearance of collagen fibers; coalescence occurs on piling. In soaking, the fibers become thicker with time. On liming for 24 to 120 hr. the fibers of steerhide increase in thickness from 47 to 58 microns, but in the painting process the fiber thickness decreases progressively to 33–24 microns after 12–18 hr. in paint. After lactic acid deliming, the separation of fibers into fibrils is indistinct. After bating, the fibers are separated, and stain red with van Gieson stain (yellow on grain and flesh) and are a little thinner. The fibers become thinner during pickling. During Cr tannage splitting into fibrils occurs, but these coalesce again (after drying [?]). The staining behavior towards van Gieson's stain (picrofuchsine) is different for different layers. During oil dressing, the fibers become thicker; they split to fibrils but later coalesce again. Elastin fibers can be demonstrated at all stages, including the finished leather. After liming, the cells in the hair follicles and fat glands are ill defined. After deliming with $NaHSO_3$ the fat glands shrink. Residues of hair in the follicles are visible. After deliming with lactic acid the staining of cell nuclei is less distinct. Amorphous matter in the fat glands gives the reactions of fat. The epithelial cells lining the hair follicles can still be demonstrated by staining after bating. L.M.

Measurement of High Viscosities [e.g., in Strong Tannin Solutions] by Shearing between Parallel Plates. F. E. Humphreys and N. Stone. *J. Sci. Instr.*, **34,** 26–27 (1957); *Chem. Abstr.*, **51,** 6232*h*.

Spectrophotometric Investigations of Potassium Chromium Alums. E. N. Slavnova. *Trudy Inst. Krist. Akad. Nauk S.S.S.R.*, **1956,** No. 12, 132–40; *Chem. Abstr.*, **51,** 6417*f*.

A Study of the Mechanism of Fatty Spue Formation. I. R. G. Mitton and K. G. A. Pankhurst. *J. Soc. Leather Trades' Chemists*, **41,** 128–55 (1957).—While the choice of fatliquor is important to spue formation, operations other than fatliquoring play a part in it. The means by which fatty materials migrate through leather and how this migration may be regulated were studied. Solid triglycerides and solid fatty acids migrate from the flesh surface of leather to the grain surface and on appearance are classified as spue. The conditions under which the migration occurs depend on the nature of the fatty material: triglycerides migrate to produce spue when the temperature is relatively high (40°C. for tristearin), especially in dry atmospheres; fatty acids migrate and appear as spue at temperatures lower than 20°C., particularly at high relative humidities. Fat is considered to migrate as a unimolecular layer on the fibers, the fat spreading over the surface in much the same way as it would over a water surface. The nature of the surface of the fibers is important and the various pre- and post-tanning operations were studied for influences on migration. Spue forms on vegetable leather much less readily than on chrome leather. With the latter, the final neutralizing, mordanting, and dyeing are important contributing factors. Tentative suggestions are made for alleviating spue on chrome leather. J.M.C.

Proposed Official Method for Testing the Fastness to Rubbing (Wet and Dry) of Light Leathers. J. C. Pittard (Chairman). *J. Soc. Leather Trades' Chemists*, **41,** 120–25, (1957). **Proposed Official Method for Testing the Fastness of Colored Leather to Water.** J. C. Pittard (Chairman). *Ibid.*, 125–26, (1957). **Proposed Official Method for Testing the Fastness of Colored Leather to Perspiration.** J. C. Pittard (Chairman). *Ibid.*, 127–28, (1957).—Reports of the Fastness Tests Committee. J.M.C.

Estimation of Sulfite-Cellulose Extract in Syntans. M. P. Balfe. *J. Soc. Leather Trades' Chemists*, **41,** 118–19 (1957).—The cinchonidine precipitation method for determination of lignosulfonate extract fails when applied to syntans. An approximate measure of the proportion of lignosulfonate in syntans can be obtained by determination of methoxyl content, assuming that the solid matter of lignosulfonate extract contains one-seventh of its weight as methoxyl. J.M.C.

Epoxide Resins. L. B. Bourne. *Chemistry & Industry*, **1956,** 578–79.—An address dealing with dermatitis and other toxic effects induced by epoxide resins and amine catalysts, and methods of avoiding them. H.B.M.

New Technical Indices Used in the Physical Testing of Finished Leather. V. Posa. *Bör- és Cipötechnika*, **6,** No. 1, 12–17 (1956); through *Hungarian Tech. Abstr.*, **9,** No. 1, 17 (1957).—The author describes the usual methods applied in the physical testing of finished leather and examines the ratio of stretching force to elongation in the stages of elongation. The ratio varies during the measurement of tensile strength, and a method of evaluation is presented for the modulus of elasticity from a tangent of the load-elongation graph plotted by an automatic recorder. The modulus of elasticity of vegetable-

tanned belting leather is determined by this method. The correlation between the modulus of elasticity in tension (E) and the modulus of elasticity in shear (G), $G = \frac{E}{2(1+\mu)}$ where μ is the modulus of elasticity, and between the modulus of elasticity in tension and the bulk modulus of elasticity (K), $K = \frac{3(1-2\mu)}{E}$, is derived. The initial modulus of elasticity (E_o) of belting leather is 360—550 kg/cm². On first stretching the modulus of elasticity increases and on the fifth to sixth stretching the initial modulus is 700—1180 kg/cm². On the straight and at the same time steepest section of the stretching diagram Emax equals 1000—1600 kg/cm² on first stretching. After repeated stretching the modulus of elasticity increases even above 2000 kg/cm² while the average modulus of elasticity is about 1500—2000 kg/cm².

PATENTS

Method of Treating Animal Skins. U. S. Pat. 2,781,241. Alexis E. Ushakoff, Beverly, Mass., assignor to Secotan, Inc., Somerville, Mass. Apl. Dec. 24, 1951.—The method of tanning skins consisting of extracting and replacing all the water of a water-wet skin with an inert water-miscible organic solvent, then treating the skin with an organic solvent solution of a chemical agent effective to change the degree of swelling of the skin to impart the desired texture, thereafter drying the skin, then tanning the skin in an inert organic solvent solution of a tanning agent while maintaining the skin under non-aqueous conditions until the skin is finally tanned and dry.

Leather Liquid Polish. U. S. Pat. 2,782,171. Elliott Morrill and Lawrence Newburn, Indianapolis, Ind., assignors to The Best Foods, Inc., New York, N. Y. Apl. Dec. 29, 1952.—A liquid polish for shoes and leather comprising an alkaline aqueous dispersion of about 1 to 18% by weight of a thermoplastic homopolymeric polybutyl methacrylate resin and about 0.25 to 3.5% by weight of a protein selected from the class consisting of vegetable protein and casein.

Leather Product and Method for Making Same. U. S. Pat. 2,785,086. Louis J. Strobino, Utica, N. Y. Apl. May 1, 1953.—A method of dimensionally stabilizing unfabricated tanned leather containing solid particles of a material resistant to the transmission of heat, embedded in the pores thereof which comprises applying uniform heat to both sides of the leather while the leather is free of contact with the heating means, the leather being held at temperatures of about 350° to 400° F. for from about 15 minutes to 3 minutes.

Preserving Textiles and Leather. U. S. Pat. 2,786,010. Alton T. White, Danvers, Mass. Apl. June 21, 1954.—A fungicidal impregnant comprising as the essential active ingredient 0.1% to 10% by weight of tetrachloro hydroquinone and as a solvent therefor a mono lower alkyl glycol ether.

Process for Purifying Tannic Acid. U. S. Pat. 2,787,635. Edward M. Filachione and Fred P. Luvisi, Philadelphia, Pa., assignors to the United States of America as represented by the Secretary of Agriculture. Apl. April 8, 1955. (Granted under Title 35, U. S. Code (1952), sec. 266).—The process for producing purified tannic acid comprising contacting an aqueous solution of the acid with methyl isobutyl ketone, whereby the tannic acid is dissolved in the ketone, and recovering the tannic acid from the the resulting ketone solution.

Process for Unhairing of Hides. U. S. Pat. 2,791,535. Theone C. Cordon, Philadelphia, Pa., assignor to the United States of America as represented by the Secretary of Agriculture. Apl. Aug. 4, 1955. (Granted under Title 35, U. S. Code (1952), sec. 266).—A process comprising treating a hide with an aqueous solution containing sodium chloride and amylase to unhair it.

Tanning Agents. Brit. Pat. 756,481. Cassella Farbwerke Mainkur Akt.-Ges. Apl. Jan. 15, 1954.—Hides and skins are tanned by treating with a water-soluble condensation product of methylol compounds of dicyandiamide and/or dicyandiamidine with a polyhydric alcohol prepared in an acidic medium at below 50° C. In examples, dicyandiamide and formaldehyde are heated together in water, cooled, and rescorcinol, phloroglucinol, pyrocatechol or its alkyl homologues added, followed by glacial acetic acid or ammonium chloride. The solutions may be used directly or concentrated and evaporated to the solid state. The tanning agents may be used before or after tannage with anionic tanning agents such as vegetable tannings, sulphonates and sulphite cellulose extracts.

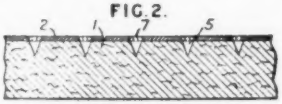
Carrotting Furs. Brit. Pat. 757,175. Deutsche Gold-Und Silber-Scheideanstalt Vorm. Roessler. Apl. Sept. 24, 1954.—In the production of felt hats, animal fibres are carrotted with an aqueous solution comprising an oxidizing agent and formamide. The oxidizing agent may be hydrogen peroxide or a per salt and the solution may also comprise nitric and/or hydrochloric acid, formaldehyde, cerium nitrate or iron salts. The fibres may be hair from rabbits or hares and may be carrotted on the pelt.

Artificial Leather. Brit. Pat. 757,814. Kotitzer Ledertuch-Und Wachstuch Werke Akt.-Ges. Apl. Mar. 31, 1954.—Artificial leather with a roughened surface having the appearance of suede, is produced by forming on a flexible support a layer of an artificial leather-like plastic including a liquid surface zone containing the plastic in latently hardenable form, distributing in the liquid surface zone particles of a solid substance insoluble therein and soluble on at least one solvent in which the plastic is insoluble hardening the liquid surface zone and finally washing out the solid substance from the plastic. The roughened surface so produced may then be buffed. A water-soluble substance such as sodium chloride, sodium sulphate, alum, an ammonium salt, urea, sugar or oxalic acid may be used as the solid substance and subsequently washed out with water. The flexible support may consist of woven or knitted fabric, felt, fleece, or paper, while a plurality of layers of film-forming natural or synthetic resin may be applied successively to the flexible sheet material each layer being solidified prior to the application of the succeeding layer and the water-insoluble

substance being applied for the final layer. The film-forming resin may be natural rubber, synthetic rubber, vinyl acetate polymers, polyvinyl chloride or vinyl chloride copolymers in the form of solutions, dispersions or pastes containing plasticizers such as dioctyl phthalate, drying oils such as linseed oil and dyestuffs.

Coated Leather; Laminated Materials. Brit. Pat. 758,065. Bellavoine, L. Apl. July 8, 1954.

FIG. 2.



—Leather 1 covered with a thin layer 2 of natural or synthetic rubber is partly perforated by conical points which form holes 5 in the leather; the holes in the rubber shrink on retraction of the point leaving only a small aperture 7. The layer 2 may be formed by coating with rubber solution or latex or by sticking on a thin rubber or synthetic rubber sheet.

Tanning. Brit. Pat. 758,674. Boehme Fett-Chemie Ges. Apl. Dec. 9, 1953. —Hides and skins are tanned by treating with a water-soluble partially condensed resin (hereinafter referred to as precondensate) obtained by reaction of an aldehyde and a nitrogenous compound, followed by vegetable and/or synthetic tanning substances of sulphite waste liquor. The precondensate may be converted into insoluble form in the skin prior to the second treatment, e.g. with alkaline or acid reagents, electrolyte solutions or by heating or may become insoluble shortly after impregnation if the skins are previously made acid. The resin tanning may be performed in the presence of a fatty tanning agent having a carbon chain with more than seven carbon atoms. Suitable precondensates are those prepared from the following components which may be reacted in neutral, acid or alkaline solution in the customary ratios. Nitrogenous compounds :— urea, thiourea, methylene di-urea, cyanamide, guanidine, alkylguanidine, dicyandiamide, dicyandiamidine and melamine. Aldehydes :— formaldehyde, acetaldehyde, acrolein and mixtures of formaldehyde and acrolein. When using a cationic precondensate, the fatty tanning agent used should preferably be cationic, e.g. animal or mineral fatty substances, synthetically produced fatty substances, mineral oils, and waxes emulsified with cationic substances; and with an anionic precondensate, the fatty tanning acid should be anionic, e.g. alkyl sulphates, alkyl sulphonates, alkyl benzene sulphonates, and sulphonated fats and oils. Suitable *p*H's for particular leathers are indicated, and in the case of vegetable tannings should be obtained by the use of organic acids. In the first example, unhaired hides are tanned with a precondensate of 1 mol. of melamine and 4 mols. of formaldehyde in the presence of aqueous mineral oil/sperm oil/dimethyl cyclohexyl dodecyl ammonium chloride emulsifier, the *p*H is adjusted to 4.6 with acetic acid and the hides are further tanned with a quebracho/mimosa/condensed hydroxyaryl sulphonic acid liquor containing a mixture of alkylsodium sulphates. In other similar examples the precondensates consist of methylene di-urea and formaldehyde and of dicyandiamide and formaldehyde.

Waterproofing Textiles, Leather and Paper. Brit. Pat. 758,987. Soc. Des Usines Chimiques Rhone-Poulenc. Apl. Aug. 5, 1954.—Fibrous organic materials, e.g. threads and fabrics of cotton, wool, cellulose acetate, viscose, vinyl compounds, superpolyamides or polyacrylonitrile, leathers during or after treating with tawing paste and papers, are waterproofed, e.g. by dipping with agitation followed by a calendering treatment, with a composition comprising an aqueous emulsion containing, calculated on the weight of the resin, oil and titanate, 20 to 61 per cent of a methylpolysiloxane resin having a CH_3 : Si ratio of 1.3 : 1 to 1.7 : 1, 25 to 50 per cent of a methylpolysiloxane oil having a CH_3 : Si ratio of 1.9 : 1 to 2.1 : 1 and 7.5 to 40 per cent of tiethanolamine titanate (*see* Group IV (a)). The emulsions may be used in conjunction with urea- or malamine-formaldehyde resins, preferably in aqueous solution, in the presence of a polymerization catalyst, or in conjunction with another waterproofing agent, e.g. an alkoxypyridium salt. Examples are given.

Waterproofing Leather. Brit. Pat. 759,395. Imperial Chemical Industries, Ltd., Hunnam, R. E., and Lumb, M. Apl. Jan. 14, 1955.—The water-repellency of leather is improved by treating it with a complex chromium compound of the Werner type in which a trivalent nuclear chromium atom is co-ordinated with a carboxylic acido group, e.g. stearato, oleato or laurato chromic chloride or nitrate, as described in U.S.A. Specifications 2,273,040, 2,356,161 and 2,524,803. The treatment may be performed by drumming the leather in an aqueous solution containing about 0.1% to 1.0% of the chromium compound. The solution, which may be prepared by diluting with water a solution of the chromium compound in e.g. isopropanol, is preferably heated to about 90—95° C. for a few minutes and allowed to cool before addition to the drum. In some of the examples the leather is dyed before treatment with the complex chromium compound.

Coated Leather. Brit. Pat. 759,860. Rohm & Haas, Co. Apl. Oct. 19, 1953. —Tanned leather is coated with a solution of a copolymer of beta-isocyanato ethyl methacrylate and stenyl acrylate in benzene (*see* Group IV (*a*)) and then oven-dried.

Flameproofing; Treating Leather. Brit. Pat. 759,863. Du Pont De Nemours & Co., E.I. Apl. Feb. 10, 1954.—Paper, textiles, wood and leather are given increased flame-resistance by impregnating with a water-soluble salt of aluminium or chromium and subsequently treating with a soluble ammonium or alkali metal salt of a polymeric phosphate which is the reaction product of a copolymer of an ethylenically unsaturated epoxy monomer and an ethylenically-unsaturated epoxy-free monomer with a phosphoric acid (*see* Group IV (a)), or by impregnating first with the soluble polymeric phosphate and then treating with the inorganic salt. Leather is treated with water-soluble salts of the above polymeric phosphates to give improved body and hand. The Specification describes the treatment of leather with an aqueous solution of the ammonium salt of the polymeric phosphate obtained by treating a copolymer of allyl glycidyl ether and vinyl acetate with orthophosphoric acid.

DIRECTIONS FOR USE:

If the leather being tanned is to receive a subsequent application of a water-repellent product fatty in nature, we recommend the use of 2% of Nopcolene R based on the pickled weight of the stock. Start the chrome tanning operation; after 30 to 45 minutes, add the Nopcolene R. Proceed in your usual manner with tanning, neutralizing, retanning and dyeing.

For leathers that are not to receive additional water-repellent fatty material, we suggest using 3 to 4% of Nopcolene R added as above. On certain types of leather, such as calfskin and sheepskin, it is possible to eliminate entirely a separate fatliquoring operation. Where an extremely soft piece of leather is desired, refatliquoring may still be done and the amount of topping oil can be reduced in direct proportion to the amount of Nopcolene R employed.

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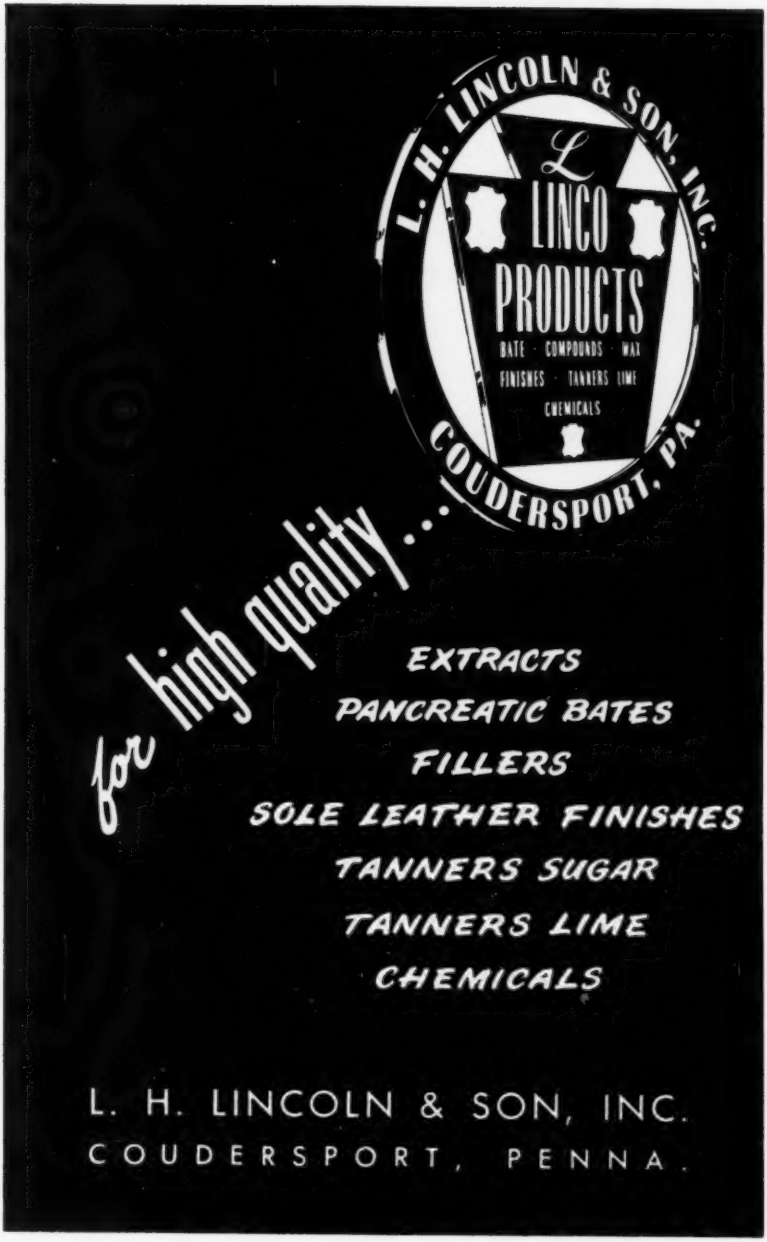
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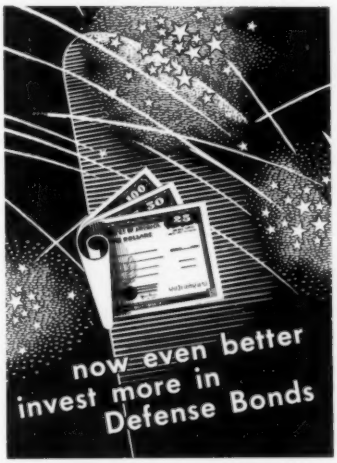

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